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SOURCES AND NATURAL REMOVAL PROCESSES FOR SOME ATMOSPHERIC POLLUTANTS

PENNSYLVANIA STATE UNIVERSITY

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This review attempts to briefly illustrate what the "state of the art" is in the recognition of the various sources and natural sinks of gaseous pollutants. The removal mechanisms include absorption by vegetation, soil, rock and water bodies, precipitation scavenging, and chemical reactions within the atmosphere. The nature and magnitude of anthropogenic and natural emissions of the gases considered (H_2S, SO_2, N_2O, NO, NO_2, NH_3, CO, O_3, and hydrocarbons), along with their ambient background concentrations and information on their major sinks identified to date, are discussed. In the case of sulfurous and nitrogenous compounds, this information has been used to prepared total geochemical cycles.

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SUMMARY

This report has attempted to illustrate what the "state of the art" is in the recognition of the various sources and sinks of gaseous pollutants. This information, summarized in Table I, outlines the nature and size of anthropogenic and natural emissions for the various gases (H_2S, SO_2, N_2O, NO, NO_2, NH_3, CO, O_3, and hydrocarbons), along with their ambient background concentrations and a listing of their major sinks identified to date. All information in this table is expanded upon in the text and is supplemented with any quantitative data on removal rates available.

The quantitative information given in this paper has, in most instances, been subject to conversion of units. The conversions were made to attain some consistency among the data and with the International System (SI) of Units. Because many people are not yet acquainted with this system, formerly used concentration dimensions, such as parts per million, are given in parentheses.

The amount of information available on gaseous source and sink strengths has blossomed the last several years. In fact, our knowledge in some areas has increased so much that much of the information in Robinson and Robbins' (1968) original work on trace gases in the atmospheric environment is now outdated. Contrary to belief of just a few years ago, for instance, it is now obvious that natural carbon monoxide emissions play an important role in determining the atmospheric background concentration of this gas.

A comprehensive search for natural pollutant removal mechanisms is presented. The following processes have been identified:

(1) foliar absorption

(2) soil absorption

(3) absorption by natural water bodies

(4) absorption by natural stone

(5) rainout and washout (scavenging)

and (6) chemical reactions in the atmosphere.

Quantitative modeling of most of these mechanisms is found to be in its infancy.

Table I. SUMMARY OF SOURCES, ANNUAL EMISSION, BACKGROUND CONCENTRATION AND MAJOR SINKS OF ATMOSPHERIC GASEOUS POLLUTANTS

Pollutant	Major Source		Estimated Emission, Kilogram		Background Concentration $\mu g/m^3$	Major Identified Sinks
	Anthropogenic	Natural	Anthropogenic	Natural		
SO_2	Combustion of coal and oil	Volcanoes	65×10^9	2×10^9	1-4	Scavenging; Chemical reactions, Soil and surface water absorption; Dry deposition
H_2S	Chemical processes; Sewage treatment	Volcanoes; Biological decay	3×10^9	100×10^9	0.3	Oxidation to SO_2
N_2O	None	Biological decay	None	590×10^9	460-480	Photodissociation in stratosphere; Surface water and soil absorption
NO	Combustion	Bacterial action in soil; Photodissociation of N_2O and NO_2	53×10^9 combined with NO_2	768×10^9	0.25-2.5	Oxidation to NO_2
NO_2	Combustion	Bacterial action in soil; Oxidation of NO			1.9-2.6	Photochemical reactions; Oxidation to nitrate; Scavenging
NH_3	Coal burning; Fertilizer; Waste treatment	Biological decay	4×10^9	170×10^9	4	Reaction with SO_x; Oxidation to nitrate; Scavenging
CO	Auto exhaust and other combustion processes	Oxidation of methane; Photodissociation of CO_2; Forest fires; Oceans	360×10^9	3000×10^9 (?)	100	Soil absorption; Chemical oxidation
O_3	None	Tropospheric reactions and transport from stratosphere	-	(?)	20-60	Photochemical reactions; Absorption by land surfaces (soil and vegetation)and surface water
Non-Reactive hydrocarbons	Auto exhaust; Combustion of oil	Biological processes in swamps	70×10^9	300×10^9	CH_4=1000 non-CH_4 <1	Biological action
Reactive hydrocarbons	Auto exhaust; Combustion of oil	Biological processes in forests	27×10^9	175×10^9	<1	Photochemical oxidation

INTRODUCTION

The last decade has witnessed an unprecedented interest and concern in the development of mathematical models for predicting air pollutant concentrations. The aim of such models is to study the complicated relationship between air quality and emission rates. The interest in air pollution modeling is based on its potential value in nearly all practical problems involving quantitative study of air quality relative to the source location and emission rates. These include the forecasting of undesirable levels of pollution, abatement strategies, long range air resources management programs and urban planning.

Because of energy shortages and use of lower quality fuels it is now more urgent that we improve our ability to forecast the consequences of increased pollutant emission. While considerable effort has been devoted to characterizing emissions from anthropogenic sources and their turbulent transport and convection, very little has been done to determine the extent of emission from natural sources and to characterize processes that clean the atmosphere. The purpose of this study is to provide quantitative information on source and removal mechanisms so that a realistic air pollution model can be constructed.

Theoretical Considerations

In general, the starting point in the development of mathematical air pollution models is the following diffusion equation:

$$\frac{\partial C_a}{\partial t} = -\underset{\rightarrow}{V}\cdot\nabla C_a + \nabla\cdot K\nabla C_a + \nabla\cdot D\nabla C_a + Q - R$$

Net rate of change at a fixed position	Net transport through system surface by convection	Net transport through system surface by turbulent diffusion	Net transport through system surface by molecular diffusion	Net gain from sources inside the volume element	Net loss by removal processes inside the volume element

where C_a is the mean concentration of pollutant a, $\underset{\rightarrow}{V}$ is the mean wind vector, K is the eddy diffusivity, D is the molecular diffusivity, Q is the rate of emission per unit volume, and R is the rate of removal per unit volume. The transport by molecular diffusion is usually ignored in atmospheric modeling, for except when close to surfaces, molecular diffusivity is much smaller than the eddy diffusivity.

The essential components of a mathematical model based on this equation are (1) a set of meteorological conditions, (2) rate of pollutant emission, and (3) rate of pollutant removal, all as functions of time and space

Pollutants may be emitted to the atmosphere from many diffuse natural and anthropogenic sources. The natural sources of many gases as shown in Table 1 far exceeds the anthropogenic sources on a global basis. However, because the gases are well distributed throughout the atmosphere their background concentration is extremely low. Anthropogenic sources of many pollutants are centered near urban complexes and therefore, their local pollutant concentrations are high and pose a major threat to the urban environment.

The removal of air contaminants from the atmosphere can take place by various mechanisms. A review of these mechanisms and their significance

was given by Robinson and Robbins (1968) and more recently by Hidy (1973). The important mechanisms are:

(1) Precipitation scavenging in which the pollutant is removed via two modes. The first is termed "rainout" which involves the absorption of gases and aerosols within the clouds. The second is called "washout" which involves both absorption and particle capture by falling raindrops;

(2) chemical reactions in the atmosphere including the stratosphere which produce either aerosols or oxidized products such as carbon dioxide and water vapor;

(3) dry deposition which involves absorption by aerosols and subsequent deposition on the earth's surface; and

(4) absorption by various substances at the earth's surface including vegetation, soil, and water bodies.

The available models, based on methods of solving the above equation, are classified as box, Gaussian plume, integrated puff, and grid models.

The box model as used by Lettau (1970) and Hanna (1973) consists of a box with its base at the ground, its sides positioned to enclose the city and its top at an assumed upper limit of vertical mixing. In this model the concentration is assumed to be independent of position, hence, it represents an average value over the volume of the system. This assumption greatly simplifies the model. However, with this simplification, the spatial resolution is completely lost. As a result, the predictions obtained by this type of model are of limited value.

The Gaussian plume models as discussed by Strom (1968) are derived with the assumption of no spatial and temporal variations in the wind.

This model does not have the flexibility for dealing with the complex atmospheric motion and its influence on the transport of pollutants. In addition, removal by various mechanisms at the earth's surface, and non-linear processes, can not be handled by this model.

In the integrated puff model as used by Robert, Croke, and Kennedy (1970) and modified by Sheih and Moroz (1973), the source term is treated as a series of puffs emitted from its origin. This model provides a more realistic simulation of atmospheric dispersion than the Gaussian plume model since it includes the local spatial and temporal effects. This model, however, fails when removal at the earth's surface and non-linear processes are significant.

Grid models are based on solving the diffusion equation by finite difference approximation (Shirl and Sheih, 1973). The only drawback of this model is a lack of computer capacity to maintain a high spatial resolution. However, the grid models have the potential of including the effect of removal by various non-linear processes and interfacial processes occurring at the system boundaries. Considering the importance of non-linear processes and surface effects in cleaning the atmosphere, it is believed that the grid model or a combination of the puff and grid models (Sheih, 1973) in the context of this study would be far more advantageous than the less comprehensive, less versatile models.

Objective

For practical purposes various assumptions have been made in solving the diffusion equation. The choice of assumption often depends on availability of data and our knowledge about the various processes which

influence the model. One assumption which is generally made is to ignore the rate of removal by various processes. This report presents an analysis of various sources and natural removal processes which should be reflected in the results obtained by air pollution mathematical modeling. Consideration of natural sources and, more importantly, removal processes in the mathematical models not only will yield more accurate results, but will provide a basis for determining the possibilities of expanding local air pollution models to regional or global scales.

This study has considered both organic and inorganic pollutants. Hydrocarbons are discussed in the organic group, while sulfurous compounds, nitrogenous compounds, carbon monoxide, and ozone are discussed in the inorganic group. This study does not even attempt to cover all the possible trace gases present in the atmosphere. Those that are discussed were chosen because their distribution and importance in the atmospheric environment are the most globally recognized. The analysis is presented in a similar form for each compound including data on ambient concentrations, sources,and mechanisms of removal.

The quantitative information given in this paper has, in most instances, been subject to conversion of units. The conversions were made to attain some consistency among the data and with the International System (SI) of Units. Because many people are not yet acquainted with this system, formerly used concentration dimensions, such as parts per million, are often given in parentheses. The concentration dimension, ppm, used in the following equations and throughout this paper is on a volume basis as is standard in the atmospheric sciences. This should not be confused with the convention in the geological sciences of expressing

ppm on the basis of mass. Following is a list of the conversions made throughout this paper.

(1) (ppm) $(.416 \times 10^{-4})$ = mol/m^3

(2) (ppm) (41.6) (molecular wt.) = $\mu g/m^3$

(3) $(\mu l/min \cdot m^2 \cdot pphm)(.17)$ = cm/sec

(4) $(\mu l/min \cdot m^2)$ (0.694×10^{-9}) = $mol/m^2 \cdot sec$

(5) $(lb/mi^2 \cdot hr)$ (0.0487) = $\mu g/m^2 \cdot sec$

(6) (lb/acre) (0.112) = g/m^2

(7) 6.02×10^{23} molecules = mol

Due to rounding off to significant figures, conversion from the numbers given in the text back to those in the original articles will not be exact.

INORGANIC GASES

The important air contaminants classified as inorganic gases include sulfur containing gases, nitrogen containing gases, carbon monoxide, and ozone. Following is a presentation of background concentrations, sources, and removal mechanisms for each gas in a similar format.

SULFUR CONTAINING GASES

The two primary sulfur containing gases present in the atmosphere are hydrogen sulfide (H_2S) and sulfur dioxide (SO_2). Hydrogen sulfide, the most reduced form of sulfur, is not considered to be an air pollutant per se, for it originates primarily from natural processes. Its importance arises from the nature of the chemical reaction it is subject to once it has been released to the atmosphere. That reaction is its rapid oxidation to sulfur dioxide As such, H_2S has often been thought of as a "natural" source of SO_2.

Accurate measurements of the background concentration of hydrogen sulfide in the atmosphere are not available Measurements over Bedford, Massachusetts, and New York City performed by Junge (1963) gave 2-20 $\mu g/m^3$ (1.4-14 ppb) Robinson and Robbins (1968) estimated H_2S concentrations in clean air to average 0.3 $\mu g/m^3$ (0.2 ppb). The National Center for Atmospheric Research (NCAR) (as cited in Kellogg, Cadle, Allen, Lazrus and Martell, 1972) has shown these measurements to be unreliable because they were made using liquid scrubbers, faulty in that they allow significant H_2S oxidation and loss. As yet, no way has been found to improve these devices

Sulfur dioxide, a primary air pollutant, has been the subject of more investigation than any other single pollutant. Observations have been made on the concentration of sulfur dioxide in the ambient atmosphere and its effect on the environment for many years. Tebbens (1968) discusses measurement of SO_2 concentrations in England made as early as 1924. Because of early recognition of SO_2 as a primary pollutant capable of inflicting severe illness or even death on humans, extensive research has increased our knowledge of the sources and sinks of this gas far more than any other pollutant.

Background concentrations of sulfur dioxide range between 1 and 4 $\mu g/m^3$ (0.4-1.5 ppb). Georgii (1970) found concentrations over the Atlantic Ocean ranging from 1-4 $\mu g/m^3$, and over Colorado from 0.5-2.0 $\mu g/m^3$ (.2-.8 ppb). Cadle et al. (1968) found values over Antarctica ranging from <1.0 to 3.2 $\mu g/m^3$ (<.4-1.2 ppb). Ambient concentrations near coal-fired power plants and petroleum refineries may reach values 1 or 2 orders of magnitude greater than background concentrations.

HYDROGEN SULFIDE

Sources

The primary source of H_2S is decaying vegetation in swamps, bogs, and other land areas. Very little is known about annual rates of H_2S production from these regions though, and up to this time such estimates are based solely on the balancing of sulfur budgets. Eriksson (1960) suggested that decaying vegetation is the source of 112×10^9 kg H_2S per year. Robinson and Robbins (1968) estimate 70×10^9 kg; more

recently Friend (1973) has estimated this source as providing 58 x 10^9 kg H_2S per year.

The oceans have been suggested as an additional source of sulfides to the atmosphere (Eriksson, 1960). Measurements though have been so inconclusive, that estimates of the magnitude of this flux [see Table VII] have been made by determining the value needed to balance a particular portion of the sulfur cycle and equating that value with the flux of $S^=$ from the oceans to the atmosphere. H_2S is also released by volcanoes but the quantity is far less than the amount of SO_2 released. Only relatively minor amounts of H_2S are released from anthropogenic sources.

Removal Mechanisms

Hydrogen sulfide is relatively insoluble in water; at 20°C and 1 atmosphere, the solubility is only 0.385g/100g H_2O. It therefore will not be readily absorbed by vegetation or bodies of water, nor will it be involved in liquid state reactions in the atmosphere. In fact, the only real mode of "removal" is the oxidation reactions it so readily becomes involved in. As a result, hydrogen sulfide has a very short residence time in the atmosphere, probably about 2 days (Hidy, 1973).

Atmospheric Reactions Involving H_2S: Hydrogen sulfide is very often thought of as a "natural" source of SO_2 because it is oxidized to the latter so rapidly after its release into the atmosphere. H_2S can be oxidized by ozone (O_3), molecular oxygen (O_2), or atomic oxygen (O).

Cadle and Ledford (1966) have shown that although the oxidation of H_2S by ozone proceeds quite slowly in a gaseous atmosphere, the reaction is catalyzed by the presence of aerosols. Hales, Wilkes and York (1969)

have established the following equation for the change in SO_2 concentration with time as a function of the concentration of both H_2S and ozone:

$$dc_{SO_2}/dt = 380 \exp(-6500/RT)\, c_{H_2S}^{0.5}\, c_{O_3}^{1.5} \frac{\mu mol}{m^3 \cdot sec}$$

where T is in degrees Kelvin

Oxidation of H_2S by atomic oxygen is limited by the presence of the latter. Atomic oxygen is formed in photochemical smog and in the stratosphere by the photolysis of ozone, and in increasing concentrations in the troposphere by the photolysis of nitrogen dioxide. The reaction to proceed first would be:

$$H_2S + O \rightarrow OH + HS$$

This is then followed by a reaction chain producing SO_2, SO_3, and sulfuric acid (Liuti, Dondes and Harteck, 1966).

SULFUR DIOXIDE

Sources

Industrial growth has caused a significant increase in the production and ultimate release of sulfur dioxide to the atmosphere Early estimates of worldwide sulfur emissions were made by Katz (1956) for each year from 1937 through 1947. For example, he estimated that global emissions for the years 1937 and 1940 were 69×10^9 kg/yr and 78×10^9 kg/yr respectively. Robinson and Robbins (1968) estimated anthropogenic activity as the source of 146×10^9 kg SO_2 each year, 70% of which they estimated was due to the combustion of coal, and

16% from the combustion of petroleum products, primarily residual fuel oil. The remaining emissions resulted from refining operations (~4%) and non-ferrous smelting (~10%). A study on anthropogenic SO_2 production by the Study of Critical Environmental Problems (SCEP) (M.I.T., 1970) concluded that globally 93 x 10^9 kg SO_2 were produced in the year 1967-1968. Kellogg et al. (1972) point out that this estimate may be low because the "emission factor" used for this global estimate is probably applicable only in the United States and will be higher in other nations which rely more heavily on fossil fuels with high sulfur contents such as coal. Kellogg et al. believe an estimate of about 100 x 10^9 kg SO_2 per year would be much more reasonable; of this, almost 94% is emitted in the Northern Hemisphere alone. Friend (1973) has estimated anthropogenic emissions of SO_2 at 130 x 10^9 kg per year.

There are, of course, natural sources of sulfur dioxide as well but the total amounts derived from these sources are extremely difficult to quantify. It is believed that most natural SO_2 is released by volcanoes. Kellogg et al. estimate that the quantity released by volcanoes is about two orders of magnitude less than the amount they estimated to be a result of man's activities (about 1.5 x 10^9 kg/yr vs. ≈1.0 x 10^{11} kg/yr). There is, as the authors point out, a good deal of uncertainty in their estimate. Stoiber and Jepsen (1973) estimated annual volcanic emissions of SO_2 to be 15 x 10^9 kg, an order of magnitude greater than the estimate of Kellogg et al.

There are no other widely accepted natural SO_2 sources. Kellogg et al. have pointed out that despite the fact that SO_2 is so very soluble in water, sea water might be a source rather than a sink if the

right physicochemical conditions prevail. Without further convincing evidence though on this subject, one should probably contend that sea water would, in toto, provide only relatively minor amounts of SO_2 to the atmosphere, if any at all.

Removal Mechanisms

Sulfur dioxide is very soluble in water; at 20°C and 1 atmosphere, the solubility is 10.8g/100g H_2O. It is also very chemically reactive and either oxidizes to sulfate or photochemically reacts with other atmospheric contaminants. Therefore, sulfur dioxide is removed from the atmosphere by various mechanisms involving water or other compounds. The major identified sinks for this gas are: precipitation scavenging, chemical conversion, and absorption by soil, water, rock, and plants. The lifetime of sulfur dioxide in the atmosphere is estimated to range between 20 minutes and 7 days (Nordo, 1973). Following is a discussion of the various mechanisms mentioned.

Vegetation: A portion of the much needed sulfur used by plants in metabolic processes has been shown by Fried(1948) to be attributed to the direct absorption of SO_2 from the atmosphere, especially in areas where the soil is sulfur deficient. The ability of the plant to utilize this sulfur effectively without damage is dependent upon the rate of absorption of SO_2 and the rate of production of sulfates. The plant can utilize this sulfur only if the production of sulfites does not exceed the capacity of the plant to oxidize the latter to sulfates.

Studies by de Cormis (1968) suggested that the extent of SO_2 absorption is directly proportional to the atmospheric SO_2 concentration

and is not influenced by the amount of sunlight. Hill (1971) investigated the uptake rates of several gases by an alfalfa canopy. His results confirmed those of de Cormis. Hill found that SO_2 was absorbed with a deposition velocity of 2.8 c./sec, given a wind velocity of 1.8-2.2 m/sec, as well as a number of other fixed variables. He did note that, in general, those gases readily absorbed by the alfalfa were those with the greatest solubility in water [see Table II and Figure 1].

Table II. SOLUBILITY IN WATER AND UPTAKE RATE OF POLLUTANTS

Pollutant	Uptake Rate in Alfalfa* $(mol/m^2 \cdot sec) \times 10^9$	Solubility at 20°C g/100 g
CO	0	0.00234
NO	2.1	0.00625
O_3	34.7	0.052
NO_2	39.6	decomposes
SO_2	59.0	10.8

*Concentration of the gas in the chamber was 2×10^{-6} mol/m^3.

Using SO_2 concentrations at 10 stations covering 5650 square kilometers near Sudbury, Canada, as measured by Dreisinger and McGovern (1970), and data from Figure 1, Hill calculated a hypothetical rate of SO_2 removal by vegetation (assuming a continuous cover of alfalfa) in this area. He indicates that the area is capable of removing 40 μg SO_2/$m^2 \cdot$sec or 560×10^3 kg/d. His analyses make a number of assumptions

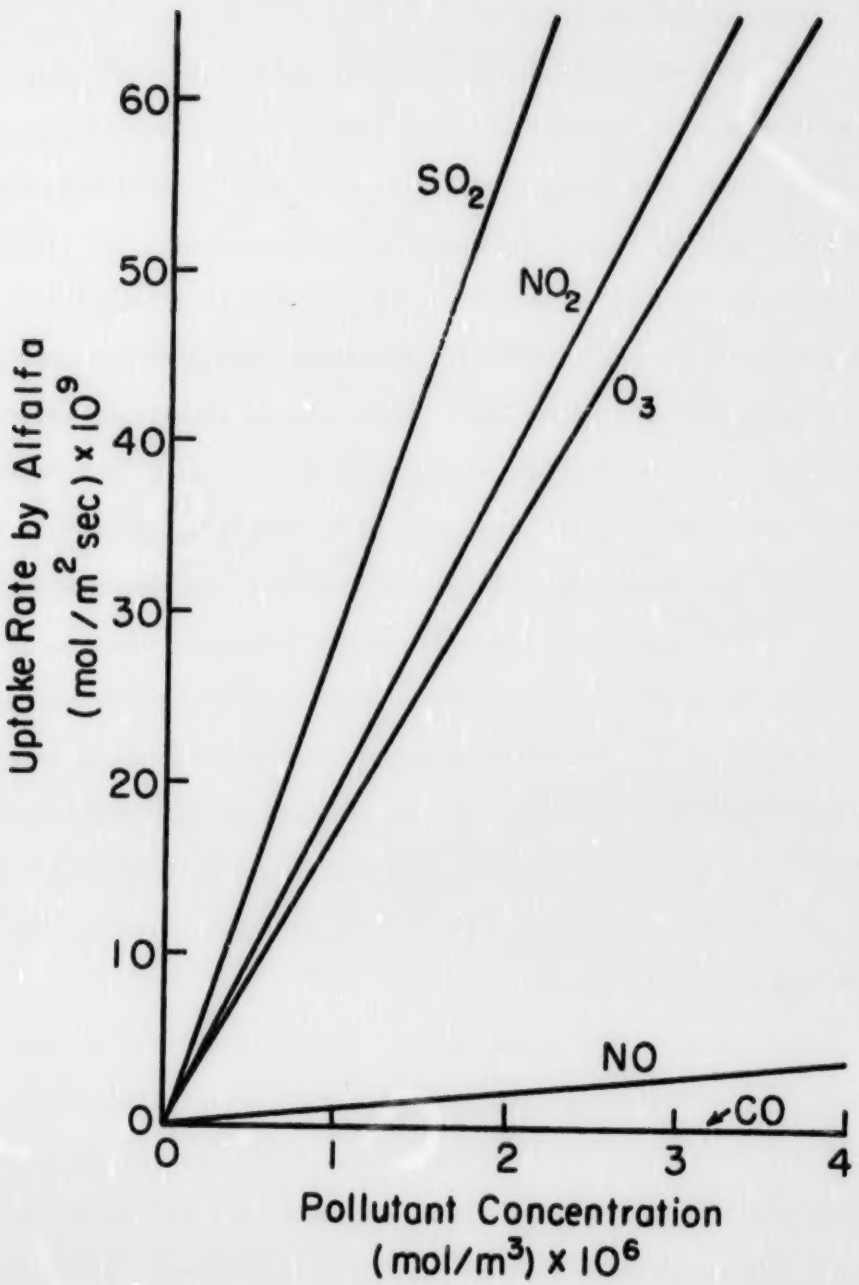

Figure 1. Uptake rates of different pollutants by an alfalfa canopy.

and yield a nice ball-park answer, but more important than the actual value is the indication it gives as to how important vegetation can be in cleansing our environment.

Factors which influence pollutant uptake by plant canopies have been discussed by Bennett and Hill (1973). In a more recent communication Bennett, Hill, and Gates (1973) present a model simulating pollutant transfer between leaves and the free air surrounding it. This model is based on the rate of exchange via a series of external and internal leaf mass transfer resistances. The model indicates the importance of gas solubility within the leaf. Thus, use of deposition velocities and vapor phase concentration alone, as done by various investigators (Owers and Powell, 1974; Shepherd, 1974; Chamberlain, 1960; and Spedding, 1969) will be inadequate for the prediction of uptake rates of a gas by plants. In addition, variables which influence momentum and mass transfer boundary layer thickness, such as wind velocity and gas diffusivity, are shown to be important in determining the rate of pollutant uptake by plants. One should bear in mind from known mass transfer theories that the shape of the plant and leaf would influence the rate of uptake as well. The effect of shape, however, has not been tested or determined.

Estimates of the amount of SO_2 removed each year by vegetal absorption vary greatly. Eriksson's (1963) cycle estimates 75×10^9 kg SO_2-S are removed in this manner. Junge (1963) estimates 70×10^9 kg SO_2-S, Robinson and Robbins (1968) estimate 26×10^9 kg SO_2-S, Kellogg et al. (1972) estimate 15×10^9 kg SO_2-S, and Friend (1973) also estimates that 15×10^9 kg SO_2-S are absorbed by vegetation each year.

The designation "SO_2-S" is a means of expressing the amount of SO_2 present as its equivalent elemental sulfur weight.

Soil: Recent studies have shown that soils are capable of absorbing significant amounts of sulfur dioxide. In 1936, Vandecaveye and associates (as cited in Bohn, 1972) noted that acid soils absorb only small quantities of SO_2. Terraglio and Manganelli (1966), in studies of two soil types, found not only that SO_2 was more readily absorbed by soil with a higher moisture content, but that the reaction also appeared to be dependent upon the pH of the soil, more SO_2 being absorbed in the soil where the pH was greater. It is, of course, not that simple. The degree of absorption is also dependent upon such factors as the mineral and organic content of the soil, soil structure, ion-exchange capacity and porosity. Faller (1968), as cited in Seim (1970), found that the oxidation (a word Faller uses as synonymous with absorption) of SO_2 was greatest in soils with the highest base saturation, other factors being equal. Faller and Herwig (1970) suggest that the amount absorbed is related to the exhangeable alkali and alkaline earth cation content, and what is absorbed is converted to H_2SO_4 when the water content of the soil is sufficient ($\geq$20%).

Experiments performed by Seim (1970) showed that soils can be important media for absorbing SO_2. He found that the amount of sulfur absorbed by the 0-2 cm depth segment of a particular dry silt (Fayette soil, analysis in his text) exposed to air containing 3720 $\mu g\ SO_2/m^3$ for 24 hours was equivalent to 10.6 g/m^2. He does note that it is questionable whether the soil can maintain this absorption rate for

extended periods of time, but it might be possible if sulfate is continually removed from the soil by leaching and/or crop uptake.

Smith et al. (1973) showed that soils of varying pH, organic carbon content, and sand, silt and clay content all readily absorbed sulfur dioxide. In a chamber containing air with an initial SO_2 concentration of 270,000 $\mu g/m^3$ (100 ppm), all six soils reduced the SO_2 content in the air by 95% in less than or equal to one minute when the soils were dry, and in less than one-half minute when the soils were 50% saturated. Sterilization of the soils caused no significant change in their SO_2 uptake ability. The removal mechanism is therefore probably not biological. Like Seim, Smith et al. suggest that the SO_2 absorbed is oxidized to sulfate which may then be subject to leaching and/or plant uptake. If the sulfate content in the soils is thereby reduced, the soils may maintain their SO_2 absorption capacity. This hypothesis has not yet been investigated.

Deposition velocities have often been used to determine the removal of SO_2 from the air above soils and vegetation. From the data available in the literature, deposition velocities for soils appear to be less than those for vegetation.

Seim obtained deposition velocities for SO_2 of approximately 0.2 cm/sec for all the soils he investigated. Chamberlain (1960) reported values of 0.3 and 0.7 cm/sec for average data over Great Britain. For combined soils and plants, Chamberlain used a value of 1.8 cm/sec. Spedding (1969) calculated a maximum deposition velocity of 1.5 cm/sec for plants. Owers and Powell (1974) calculated a mean deposition velocity of 0.8 cm/sec over Great Britain assuming the countryside is all grassland.

Seim points out that "if these values are valid and the 0.2 cm/sec value obtained for soils alone in this study should prove to be valid over a wide range of climatic conditions, the conclusion which must be drawn is that plants account for greater absorption of SO_2 from the atmosphere than soil".

Estimates on the amount of SO_2 that is absorbed by soils are lacking and, for the most part, missing from most sulfur cycles that have been compiled. Unless this process has been taken into account in estimating the total sulfur deposited by dry deposition on the land surface then one must conclude that there is an obvious omission in the cycles. Eriksson (1963) estimated that 75×10^9 kg/yr of dry deposition sulfur goes through plants into the soil while 25×10^9 kg/yr are directly absorbed by the soil. Abeles et al. (1971), based on experiments they themselves ran, concluded that soils of the United States are capable of removing 4×10^9 kg of SO_2 per year.

Rock: Living matter has a threshold limit of tolerance to pollutants, below which no injury will occur, and, in fact, the substance might actually benefit from the presence of that pollutant. Rock reacts with pollutants such as SO_2, at all concentrations. The results of these reactions may not be visible for quite some time, for the effects are cumulative. The extent of breakdown of the rock is therefore less a product of the momentary concentration of the pollutant than the uptake per unit time on a unit area of the material (Luckat, 1973).

The effects of SO_2 on frescoes, monuments and other edifices have been most pronounced over the last century, expecially in Europe where high-sulfur coal and oil are used as heating fuels. The basic

destructive reaction is that of sulfuric acid ($SO_2 + 1/2\ O_2 + H_2O \rightarrow H_2SO_4$) on the carbonate matrix of limestone and sandstone in the presence of moisture. Spedding (1969b) has shown that as the relative humidity in the air increases, the SO_2 uptake rate by oolitic limestone increases significantly (Table III).

Table III. UPTAKE OF SO_2 BY OOLITIC LIMESTONE

Relative Humidity %	SO_2 concentration $\mu g/m^3$	Time of exposure min.	Uptake $\mu g\ SO_2/cm^2$ of surface	Uptake rate $\mu g/cm^2 \cdot d$
11	360	20	0.069	5.0
13	280	40	0.061	2.2
79	100	48	0.24	7.2
81	370	10	0.28	40.3

The product of the reaction between sulfuric acid and the carbonate matrix is gypsum if sufficient evaporation occurs:

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2$$

Because the calcium carbonate is slowly being replaced by gypsum the rock would be subject to increased weathering rates due to:

(1) an enhanced chemical disintegration caused by the much greater solubility of gypsum in water than calcium carbonate. The newly formed mineral would be subject

to dissolution in water with accompanied leaching out of the rock, and

(2) an enhanced physical disintegration caused by the almost two-fold volume expansion in the rock accompanying the formation of gypsum.

Other properties such as the density and porosity of the rock are also important and affect the amount of weathering to be expected in a rock per unit uptake rate; a rough, porous, lime-cemented sandstone would be expected to weather faster than a smooth, dense limestone (Luckat, 1973).

To determine whether the absorption of SO_2 by sedimentary rocks would constitute a significant sink for SO_2, a number of assumptions were made:

(1) Knowing that approximately 30% of the total earth's surface area of about 5×10^{14} m^2 was land (Holmes, 1965), and assuming that perhaps 5% of the land surface had exposed rock (F. E. Wickman, 1974), and of this approximately 75% is sedimentary (Leet and Judson, 1965), it was calculated that about 1% of the total earth's surface was covered with rock capable of absorbing SO_2.

(2) Luckat (1973) and Spedding (1969b) found SO_2 absorption rates ranging from 5-200 $mg/m^2 \cdot d$ in sandstone and limestone, respectively. Luckat's measurements were taken in a highly industrialized region of Germany; Spedding's measurements were made with SO_2 concentrations approximately 100 times greater than the average world-wide background concentration.

For this calculation, the lower limit of 5 $mg/m^2 \cdot d$ was used.

From these values it was calculated that approximately 9×10^9 kg SO_2/yr or 4.5×10^9 kg S/yr could be removed by stone under these optimal and exaggerated conditions. Comparison of this value with those in Table V shows this value to be considerably smaller than that of any other natural SO_2 sink.

There are many problems related with making any such estimate as was done above. First of all, any estimate of the total percentage of the earth's surface which has exposed rock is entirely speculative at this point in time because geological maps are not available for all parts of the world. Then again, there is the problem of defining an outcrop and mapping it in its strictest sense; that is, mapping the outcrop without magnification and without the inclusion of soils or detritus as part of the outcrop. There is also the fact that not all the sedimentary rock that is exposed is sandstone or limestone; much of it is shale or mudstone or something of similar density which would probably not absorb SO_2 to any extent. Finally, the areas where most of the rock does outcrop would be in areas where the SO_2 level would probably be quite low. It can therefore be assumed that rock constitutes a negligible sink for SO_2 on a global scale.

Water Bodies: Theoretical arguments in support of the contention that sea water is capable of absorbing significant quantities of sulfur dioxide from the atmosphere first appeared in a paper by Liss (1971) and were modified by Liss and Slater (1974). Briefly, the rate at which a gas is exchanged across an interface can be obtained by using a mass

transfer coefficient, k, having velocity dimensions and defined as:

$$k = \frac{\text{flux of gas}}{\text{concentration difference over a thickness, z}} \qquad (1)$$

The overall mass transfer coefficient, K, based on liquid (ℓ) or gas (g) phase concentrations is related to individual mass transfer coefficients by the following equation

$$\frac{1}{K_\ell} = \frac{1}{k_\ell} + \frac{1}{Hk_g} \text{ or } \frac{1}{K_g} = \frac{1}{k_g} + \frac{H}{k_\ell} \qquad (2)$$

$$R_\ell = r_\ell + r_g \text{ or } R_g = r_\ell + r_g \qquad (3)$$

where k_ℓ and k_g are the mass transfer coefficients for the gas and liquid phases respectively. The terms r_ℓ and r_g are measures of the resistances in the liquid and gas phases and are obtained from the reciprocals of individual mass transfer coefficients. The Henry's law constant, H, is defined as:

$$H = \frac{\text{equilibrium concentration in gas phase (g/cm}^3 \text{ air)}}{\text{equilibrium concentration of un-ionized dissolved gas in liquid phase (g/cm}^3 \text{ } H_2O)} \qquad (4)$$

and differs for every gas.

Whether the net transfer of a gas is controlled by the liquid phase or gas phase is determined by the ratio of the resistances of the gas to liquid phase (r_g/r_ℓ). For most gases (N_2O, CH_4 and CCl_4 to name just a few) $r_g/r_\ell < 1$, and transfer is controlled by the liquid phase.

Sulfur dioxide transfer though is evidently controlled by the gas phase; that is $r_g/r_\ell >> 1$. For water vapor $r_\ell = 0$ and the exchange across the interface is controlled by processes in the gas phase. With the knowledge of mass transfer coefficients for one contaminant, one can approximate the mass transfer coefficients for other contaminants.

Liss and Slater (1974) used the mass transfer coefficient for water vapor to calculate the overall mass transfer coefficients for a number of gases crossing the air-sea interface. The results are given in the following table:

Table IV. MASS TRANSFER COEFFICIENT FOR A NUMBER OF GASES CROSSING THE AIR-SEA INTERFACE

Gas	k_g cm/sec	k_ℓ cm/sec	H	r_g/r_ℓ	K* cm/sec
SO_2	0.45	9.6	3.8×10^{-2}	573	0.45 (g)
N_2O	0.53	0.0055	1.6	6.6×10^{-3}	0.0055 (ℓ)
CO	0.67	0.0055	50	1.7×10^{-4}	0.0055 (ℓ)
CH_4	0.885	0.0055	42	1.5×10^{-4}	0.0055 (ℓ)
H_2O	0.833	∞	---	∞	0.83 (g)

*The overall exchange constant, K, is expressed on either a gas (g) or liquid (ℓ) phase basis.

Liss (1971) first showed that the exchange of SO_2 with aqueous solutions was a function of pH (see Table V). A chemical enhancement factor, α, equals the ratio of the k_ℓ values for a reactive and an

Table V. CALCULATION OF THE RATIO OF THE GAS TO THE LIQUID PHASE RESISTANCE

pH	α	$k_{\ell(SO_2)}$ cm/sec	$(1/k_{\ell(SO_2)})=r_\ell$ sec cm^{-1}	$(1/Hk_{g(SO_2)})=r_g$ sec cm^{-1}	r_g/r_ℓ
2	2.7	0.0075	130	32	0.25
2.8	11.7	0.0325	30.8	32	1.04
3	18.0	0.050	20.0	32	1.60
4	169	0.469	2.1	32	15.29
5	1,376	3,822	0.26	32	123.1
6	2,884	8.011	0.125	32	256.0
7	2,966	8.239	0.121	32	264.5
8	2,967	8.242	0.121	32	264.5
9	2,967	8.242	0.121	32	264.5

inert gas exchanging under identical conditions. As can be seen, above a pH of 2 8 the gas phase resistance becomes dominant, and therefore the exchange of SO_2 with natural waters (pH 4-9) is controlled by the gas phase. At a pH of 8 (approximately that of sea water) the gas phase resistance has increased to more than 99 percent of the total resistance. Brimblecombe and Spedding (1972) experimentally confirmed these results of Liss. Liss and Slater (1974) suggest that the exchange of other gases, such as NH_3, SO_3 and HCl which also are very soluble and undergo rapid hydration reactions, might also be controlled by the

resistance of the gas phase. It should be pointed out that the difference in the values of the ratio r_g/r_ℓ for SO_2 at a pH of about 8 between Tables IV and V is due to (1) a smaller chemical enhancement factor used in calculations for Table IV yielding a slightly larger $k_{\ell(SO_2)}$ value, and (2) a difference in calculating the value of $k_{g(SO_2)}$. Whereas Liss and Slater derived $k_{g(SO_2)}$ by correcting the value of $k_{g(H_2O)}$ by a factor equal to the ratio of the square roots of the molecular weight of water to the molecular weight of SO_2 (as in Table IV), Liss (1971) had assumed that $k_{g(H_2O)} \approx k_{g(SO_2)}$.

Spedding (1972) collected samples of sea water and, by measuring the amount of SO_2 absorbed by the water from an atmosphere containing SO_2, determined the deposition velocity of SO_2 over sea water. He found that the deposition velocity of SO_2 increased linearly as the gas flow rate increased. The natural buffering capacity of sea water prevented any drop in the pH (≈8), and thus would not limit the amount of SO_2 absorbed. Earlier, Terraglio and Manganelli (1967) had found a rapid and substantial decrease in pH when SO_2 was absorbed by distilled water.

Most data on SO_2 solubility in the literature have been determined when atmospheric SO_2 concentrations in the experimental chambers far exceeded those found in ambient air. Hales and Sutter (1973) worked towards closing this obvious gap by running a number of experiments to help "quantify the relationships between SO_2 solubility, concentration, and hydrogen-ion impurity at levels normally encountered in nature." The dissolution of SO_2 was assumed to proceed according to the reactions set forth by Falk and Giguere (1958):

$$SO_{2_g} + H_2O \rightleftarrows SO_{2_{aq}} + H_2O \quad (5)$$

$$SO_{2_{aq}} + 2H_2O \rightleftarrows H_3O^+ + HSO_3^- \quad (6)$$

$$HSO_3^- + H_2O \rightleftarrows H_3O^+ + SO_3^{2-} \quad (7)$$

The second ionization (reaction 7) was assumed to be negligible.

Based upon the first two of the above reactions, Hales and Sutter derived an "extrapolation equation, relating the concentration of total dissolved SO_2 in water (c_{SO_2}) to airborne concentration and solution acidity" as follows:

$$c_{SO_2} = [SO_2]_{aq} + [HSO_3^-] = \frac{[SO_2]_g}{H} + \frac{-[H_3O^+]_{ex} + \sqrt{[H_3O^+]_{ex}^2 + 4\ K_1\ [SO_2]_g/H}}{2} \quad (8)$$

where those terms bracketed are concentrations in moles per liter and $[H_3O^+]_{ex}$ is the "excess" hydrogen ion concentration, defined as the concentration of hydrogen ion in solution present due to sources other than the dissolving of SO_2. K_1 is the equilibrium constant for reaction (6) and H is the Henry's law constant. Extrapolation of SO_2 solubility data from Johnstone and Leppla (1934) down to low ambient SO_2 concentrations show deviations ranging from 0.7 to 21.2% of those by Hales and Sutter. In general, the percent deviation increased as the concentration of SO_2 in the gas phase decreased. The authors suggest that even though this deviation does exist, the ability of equation (8) to predict low SO_2 concentration solubility appears excellent and they recommend its use whenever low concentration solubility data are needed.

A more exact equation for determining the total dissolved SO_2 in water can be derived based on the solution equilibria involved. The resulting equation not only takes into consideration the pH of the solution and the atmospheric partial pressure of the gas, P_{SO_2}, but applies to different aqueous phase conditions, including both sea water and rain water. Also it eliminates the use of the often confusing and now outdated hydronium ion (H_3O^+). The dissolution and dissociation reactions for SO_2 in water are more correctly written (Scott and McCarthy, 1967)

$$SO_{2_g} + H_2O \rightleftarrows SO_2 \cdot H_2O \tag{9}$$

$$SO_2 \cdot H_2O \rightleftarrows H^+ + HSO_3^- \tag{10}$$

$$HSO_3^- \rightleftarrows H^+ + SO_3^= \tag{11}$$

In the equations which follow the activity, a, of the aqueous species is denoted by brackets [ ]. The activity and the molality of a species are related by the activity coefficient, $a = m\gamma$. In dilute solutions the molality (moles/1000g H_2O) of a species is approximately equal to its molarity (moles/ℓ H_2O). Rigorously the activity is dimensionless but for calculational purposes it may be taken to have the dimensions of molality or molarity with the activity coefficient being dimensionless.

Johnstone and Leppla (1934) and Scott (1964) show that reaction (9) follows Henry's law for dilute solutions up to concentrations of at least one molar. Thus,

$$H = \frac{[SO_2 \cdot H_2O]}{P_{SO_2}} \tag{12}$$

where $[SO_2 \cdot H_2O]$ is the activity of solvated sulfur dioxide and P_{SO_2} is the SO_2 partial pressure in atmospheres. The defining equations for the ionization constants are:

$$K_1 = \frac{[H^+]\ [HSO_3^-]}{[SO_2 \cdot H_2O]} \tag{13}$$

$$K_2 = \frac{[H^+]\ [SO_3^=]}{[HSO_3^-]} \tag{14}$$

Using equations (12), (13) and (14), a molal mass balance for the system can be written

$$\Sigma m_{SO_2} = m_{SO_{2_{aq}}} + m_{HSO_3^-} + m_{SO_3^=} \tag{15}$$

wherein,

$$m_{SO_{2_{aq}}} = \frac{H\ P_{SO_2}}{\gamma_{SO_{2_{aq}}}} \tag{16}$$

$$m_{HSO_3^-} = \frac{K_1\ H\ P_{SO_2}}{\gamma_{HSO_3^-}\ [H^+]} \quad \text{and} \tag{17}$$

$$m_{SO_3^=} = \frac{K_2\ K_1\ H\ P_{SO_2}}{\gamma_{SO_3^=}\ [H^+]^2} \tag{18}$$

Substituting the values for the molality for each of these species into equation (15), the following general formula for the concentration of dissolved SO_2 is derived:

$$\Sigma m_{SO_2} = H\, P_{SO_2}\left(1/\gamma_{SO_2\,aq} + K_1/\gamma_{HSO_3^-}[H^+] + K_2\, K_1/\gamma_{SO_3^=}[H^+]^2\right) \qquad (19)$$

The definition of pH is

$$pH = -\log\,[H^+]$$

Therefore, by convention, in equations the activity of the hydrogen ion can be written $[H^+] = 10^{-pH}$ as desired.

For use in predicting SO_2 solubility, equation (19) requires values for H, K_1, K_2 and the three activity coefficients in addition to the pH and the SO_2 partial pressure. Scott and Hobbs (1967) give H = 1.24, K_1 = 0 0127, and $K_2 = 6.24 \times 10^{-8}$ at 25°C. Corresponding data at other temperatures are given by Johnstone and Leppla (1934). One case of considerable interest is the absorption of SO_2 in sea water. Activity coefficients of aqueous sulfite species, $SO_2 \cdot H_2O$, HSO_3^-, and $SO_3^=$ in sea water are not available. However, Reardon (1974) determined activity coefficients for the analogous carbonate species and also sulfate ion in sea water. From a point of view of similarity of species and coherence among the variables, the sulfate activity coefficient is rejected in favor of use of the carbonate species activity coefficients. Hence,

$$\gamma_{SO_2\,aq} \simeq \gamma_{H_2CO_3^\circ} = 1.19$$

$$\gamma_{HSO_3^-} \simeq \gamma_{HCO_3^-} = 0.67$$

$$\gamma_{SO_3^=} \simeq \gamma_{CO_3^=} = 0.19$$

By substituting these values into equation (19), and assuming that sea water has a pH of 8.1, equation (13) reduces to

$$\Sigma m_{SO_2} = 8.42 \times 10^{7} P_{SO_2} \qquad (20)$$

where the amount of dissolved SO_2 is seen to be a linear function of the atmospheric partial pressure of SO_2.

The minimum background concentration of SO_2 is 1 $\mu g/m^3$ which corresponds to 3.8×10^{-10} atmospheres SO_2 partial pressure. From equation (20) the amount of SO_2 dissolved in sea water at equilibrium would be 3.2×10^{-2} mol/ℓ. As an upper limit one might consider ambient SO_2 concentrations found by Luckat (1973) in highly industrialized sections of Germany. The observed 360 $\mu g/m^3$ is equivalent to $P_{SO_2} = 1.4 \times 10^{-7}$ atm. In equilibrium with such an atmosphere sea water would absorb 11.6 mol SO_2/ℓ. This molarity is an order of magnitude higher than that where Henry's law is known to hold. Thus, the predictive equation might fail under these circumstances.

When the dissolution of SO_2 takes place in rain water, the activity coefficients required for equation (19) may be assumed equal to unity because the ionic strength of rain water (a measure of the interionic effect resulting primarily from electrical attraction and repulsions between the various ions) would be very low, probably on the order of 10^{-4}. Therefore, equation (19) reduces to

$$\Sigma m_{SO_2} = P_{SO_2} \left(1.24 + \frac{1.58 \times 10^{-2}}{[H^+]} + \frac{9.83 \times 10^{-10}}{[H^+]^2}\right) \qquad (21)$$

In this case the hydrogen ion activity is dependent upon the amount of SO_2 absorbed and cannot be specified a priori. The charge balance for the dissolution and dissociation reactions of SO_2 in water is

$$[H^+] = [HSO_3^-] + 2[SO_3^=] + [OH^-]$$

By substituting in the respective expressions for the $[HSO_3^-]$ and $[SO_3^=]$ as given by equations (12, 13, and 14), and setting $[OH^-] = 10^{-14}/[H^+]$, an expression is derived for the partial pressure of SO_2 as a function of $[H^+]$ as follows:

$$P_{SO_2} = \frac{[H^+]^3 - 10^{-14}\,[H^+]}{1.58 \times 10^{-2}[H^+] + 1.97 \times 10^{-9}} \qquad (22)$$

Choosing an initial value for the $[H^+]$, and substituting that value into equation (22), a corresponding value for P_{SO_2} (atm) can be found. These values for P_{SO_2} and $[H^+]$ are then in turn substituted into equation (21) to find the amount of total dissolved SO_2.

In pure rain water the pH is 7.0. Any SO_2 which dissolves would produce an acid solution and a drop in pH. Thus, for pH = 7, $P_{SO_2} = \Sigma m_{SO_2} = 0$. For a pH of 5, P_{SO_2} and Σm_{SO_2} are calculated to be 6.3×10^{-9} atm and 1.0×10^{-6} mol/ℓ, respectively. For a pH of 3, $P_{SO_2} = 6.35 \times 10^{-5}$ atm and $\Sigma m_{SO_2} = 1.1 \times 10^{-3}$ mol/ℓ. Clearly as P_{SO_2} increases, the amount of dissolved SO_2 increases and the pH decreases. The dissolved SO_2 predicted by equations (21) and (22) agree excellently with the experimental data of Hales and Sutter (1973) and Terraglio and Manganelli (1967).

Estimates of the amount of SO_2 absorbed annually by the oceans indicate the importance of this sink. Liss and Slater (1974) estimate this SO_2 flux at 1.5×10^{11} kg/yr based upon their own calculations. Their estimate is in good agreement with those of Eriksson (1963) (2×10^{11} kg/yr) and Robinson and Robbins (1968) (0.5×10^{11} kg/yr), but is lower than that determined by Spedding (1972) (9.6×10^{11} kg/yr). Liss and Slater explain that this discrepancy is due to a 3 $\mu g/m^3$ difference in the mean atmospheric SO_2 concentration used by each and because Spedding's value for the total resistance of the gas phase ($1/K_g$) was much lower. As noted earlier, Kellogg et al. (1972) consider the net flux of SO_2 from air to sea to be negligible, based on observations made by Pate et al. (personal communication to Kellogg et al.) that in some areas, where the equilibrium vapor pressure of SO_2 in surface waters exceeds the partial pressure of SO_2 in the air above it, the ocean might actually be a source of SO_2. Although this condition may exist locally, on a global basis it would make far more sense to consider the ocean as a sink in light of the high solubility of SO_2 in water. Also, whereas laboratory experiments have shown that the solution and rate of oxidation of SO_2 to sulfate in distilled water is limited by the pH as the solution becomes more acidic (Terraglio and Manganelli, 1967), this would not be the case in the ocean (Spedding, 1972). The ocean has a natural buffer capacity that maintains the pH at about 8.1. Therefore, pH would not be a limiting condition in sea water and so it should have the capacity to constantly absorb SO_2. This seems consistent with the discovery of Liss (1971) and Liss and Slater (1974) that it is the gas phase and not the liquid phase that limits the transfer of SO_2 across the air-sea interface.

Washout and Rainout of SO_2: The major portion of SO_2 present in the atmosphere is probably removed by the processes known as rainout and washout. Rainout involves the scavenging of SO_2 and sulfate particles within the clouds while washout is the removal of these sulfur compounds below cloud level via precipitation. The SO_2 scavenged will undergo a series of reactions, some catalytic, and ultimately form H_2SO_4 drops or a sulfate salt. The following paragraphs, due to their nature, might just as well be included in the section on chemical reactions involving SO_2 in the atmosphere, but they are included here so the reader can best follow the sequence of events from the time the gaseous SO_2 reacts with water vapor in the atmosphere until the sulfate salts are removed by precipitation or dry deposition.

From the time SO_2 is absorbed by cloud droplets it is both ionized and oxidized by reactions (9), (10) and (11) shown in the previous section and (23)and (24) as follows (Miller and de Pena, 1972):

$$SO_2 \cdot H_2O + OH^- = HSO_3^- + H_2O \qquad (23)$$

$$SO_3^= + 1/2\ O_{2\ dissolved} \rightarrow SO_4^= \qquad (24)$$

It is obvious then that any SO_2 absorbed by water droplets will not only contribute to the sulfate content of rainwater but will also cause a decrease in the pH of the rain. The pH of rain usually ranges from 5-6 but can drop down to about 4 in areas where large amounts of SO_2 are present in the atmosphere. Because the pH drops, reaction (23) is important only in the first few seconds. Perhaps it would be easier to visualize if the sequence above is given as the net reaction:

$$SO_2 + H_2O + 1/2\ O_{2\,dissolved} \rightarrow SO_4^{=} + 2H^{+} \qquad (25)$$

Because the oxidation of SO_2 in the liquid phase does not occur at a rate fast enough to account for the sulfate content found in rain, investigations were undertaken to find an effective catalyzing agent. Experiments have shown that of all tne metals found in the atmosphere, Mn salts were the most effective in promoting SO_2 oxidation (Junge and Ryan, 1958; Johnstone and Coughanowr, 1958; and Matteson et al., 1969). Although Mn salts are the best known catalyst for SO_2 oxidation, the concentration of these salts in the atmosphere is still not great enough to account for the sulfate content in rain. Recent investigations though have shown that when ammonia is present the rate of sulfate production in solution is greatly enhanced (van den Heuval and Mason, 1963; Scott and Hobbs, 1967; and Miller and de Pena, 1972).

The results of Scott and Hobbs'initial study as to how the concentrations of SO_2 and NH_3 effect the amount of $SO_3^{=}$ produced and the pH of the precipitation are shown in Table VI. The results are given in terms of the $SO_3^{=}$ concentration because the rate of $SO_4^{=}$ production depends only on $[SO_3^{=}]$ (reaction 22). The first line of Table VI gives the initial values of the pH and the $SO_3^{=}$ concentration corresponding to partial pressures of SO_2 and NH_3 typical of those found in the Earth's atmosphere, namely 20 $\mu g/m^3$ (7×10^{-9} atm) and 5 $\mu g/m^3$ (7×10^{-9} atm), respectively. The following lines show the effect of varying the concentrations of SO_2 and NH_3. One can see that more sulfite is produced given the same SO_2 concentration when NH_3 is present. Also, as the concentration of NH_3 increases so does that of the sulfite produced.

Table VI. INITIAL VALUES OF THE pH AND THE CONCENTRATION OF SULFITE ($SO_3^=$) ION FOR VARIOUS PARTIAL PRESSURES OF SO_2 AND NH_3

Partial pressure of SO_2 (atm)	Partial pressure of NH_3 (atm)	Initial pH	Initial concentration of $SO_3^=$ (moles liter^{-1})
7×10^{-9}	7×10^{-9}	6.34	3.4×10^{-5}
7×10^{-9}	0	4.97	6.0×10^{-8}
1.4×10^{-8}	7×10^{-9}	6.21	3.6×10^{-5}
7×10^{-9}	1.4×10^{-8}	6.48	6.2×10^{-5}
5×10^{-6}	5×10^{-6}	6.35	2.4×10^{-2}
5×10^{-6}	0	3.55	6.2×10^{-8}

One can also see the effect that the presence of NH_3 has on the pH. When no ammonia is present the pH is highly acidic. When present though, the hydroxyl ion produced upon the dissolution of ammonia in water tends to neutralize the hydrogen ions produced by the dissolution of SO_2. Therefore when ammonia is present the pH remains a little over 6. These values have all been attained with CO_2 present in the gas phase at an average concentration of 362,000 $\mu g/m^3$ (311 ppm). Therefore the acid pH is a result of dissolution of CO_2 as well as SO_2, but the variability is mainly attributable to SO_2 and NH_3 concentrations.

Field investigations by Beilke and Georgii (1968) indicated that the absorption of gaseous SO_2 by rainout and washout accounted for 75% of the sulfate content in rain water and that scavenging of sulfate

particles contributed only 25%. The model formulated by Miller and de Pena contradicts those measurements of Beilke and Georgii. Miller and de Pena show that the sulfate content of rainwater is much more dependent on the scavenging of particles rather than SO_2. In their model, the sulfate content of rain water near a highly concentrated SO_2 plume of only moderate particle concentration, showed that the contribution of SO_2 toward the total sulfate concentration was 4 times less than that of sulfate particles. Miller and de Pena's model makes more sense, especially because all reactions involving SO_2 in the atmosphere ultimately lead to the formation of $SO_4^=$.

Appreciable effort has been devoted to the analysis of SO_2 scavenging by rain (Engelmann, 1968; and Fuquay, 1970). Field measurements of SO_2 washout (Hales, Thorp, and Wolf, 1971) have demonstrated that there is a significant accumulation of SO_2 in the water drops, and consequently, calculations of the washout based on deposition velocities are inadequate.

A comprehensive analysis of reversible washout based on the interaction of raindrops with atmospheric contaminants has been presented by Hales (1972). This analysis indicates the use of overall mass transfer coefficients for determining the washout. From this analysis, it is apparent that the degree of success in determining washout rates depends on estimating mass transfer coefficients and solubility data. Hales used mass transfer coefficients for the limiting cases of gas phase control or liquid phase control without internal circulation within the drop to obtain the upper and lower limits of gas washout rates. Further study (Hales, Dana, and Wolf, 1973; and Hales, Wolf, and Dana, 1973) has led to the development of a mathematical model for predicting

ground level concentrations in the rain as a function of location beneath a plume under stable meteorological conditions.

Atmospheric Reactions Involving SO_2: Reactions involving SO_2 in the dry state, not unlike those discussed above for SO_2 in the wet state, are very complex. The most important reaction involved here is the photochemical oxidation of SO_2 which takes place in polluted atmospheres.

Early measurements of the rate of photo-oxidation of SO_2 made by Gerhard and Johnstone (1955) are the most widely quoted. They found the rate of SO_2 oxidation to proceed from 0.1-0.2%/hour. Recently, Cox and Penkett (1970) measured this oxidation rate in experiments using purified ambient air and found rates ranging from 0.04-0.65%/hour. Analysis of the gaseous composition in their test chamber found small amounts of hydrocarbon compounds ($.04 - 0.2 \times 10^{-4}$ mol/m^3, or, 0.1-0.5 ppm) and nitrogen oxides (<10 μg/m^3, or, <0.005 ppm), and they suggest that their presence might be responsible for the high observed photo-oxidation rates. Renzetti and Doyle (1960) had earlier suggested that the rate of photochemical aerosol formation (the end result of the photo-oxidation of SO_2) is greatly accelerated in the presence of olefinic hydrocarbons and nitric oxide. Endow, Doyle and Jones (1963) and Harkins and Nicksic (1965) have shown that the resulting aerosols consist almost entirely of sulfuric acid droplets when the relative humidity is greater than or equal to 50%.

Cox and Penkett (1971a) have given experimental evidence to support the hypothesis that low concentration olefinic hydrocarbons and nitric oxide can greatly affect the rate of SO_2 photo-oxidation in air.

Results of their experiments can be easily observed in Figure 2. The rate constant obtained for the oxidation of SO_2 in this experiment was 0.025 hr^{-1} with 40 $\mu g/m^3$ (0.03 ppm) NO and .04 x 10^{-4} mol/m^3 (.1 ppm) cis-2-pentene present. They argue that due to reduced light intensity in their chamber, their rate obtained would be analogous to a conversion rate of about 10%/hour over London. Although this conversion rate seems very high, they suggest it gives support to the oxidation rate of SO_2 of 0.65%/hour found in their earlier experiment as being more realistic for existing atmospheric conditions than those found by Gerhard and Johnstone.

Although the rate of SO_2 oxidation by ozone alone is quite slow, Cox and Penkett (1971b) found that when SO_2 was injected into a chamber containing ozone and olefins the oxidation rate was greatly enhanced. They also found that the oxidation rate, or aerosol formation, was dependent upon the nature of the olefin; the rate of aerosol production was much slower for terminally unsaturated propene and 4-methyl-1-pentene than it was for the internally unsaturated olefins, cis-2-pentene and 2-methyl-2-butene. They calculated the oxidation rate of 270 $\mu g/m^3$ (.1 ppm) SO_2 in the presence of 2 x 10^{-6} mol/m^3 (.05 ppm) ozone and olefin to be approximately 3%/hr for cis-2-pentene and 0.4%/hr for propene.

As little as is known about the oxidation of SO_2 in the troposphere, still less is known about its oxidation in the stratosphere. Cadle and Powers (1966) have suggested a possible 3-body reaction with atomic oxygen

$$SO_2 + O + M \rightarrow SO_3 + M$$

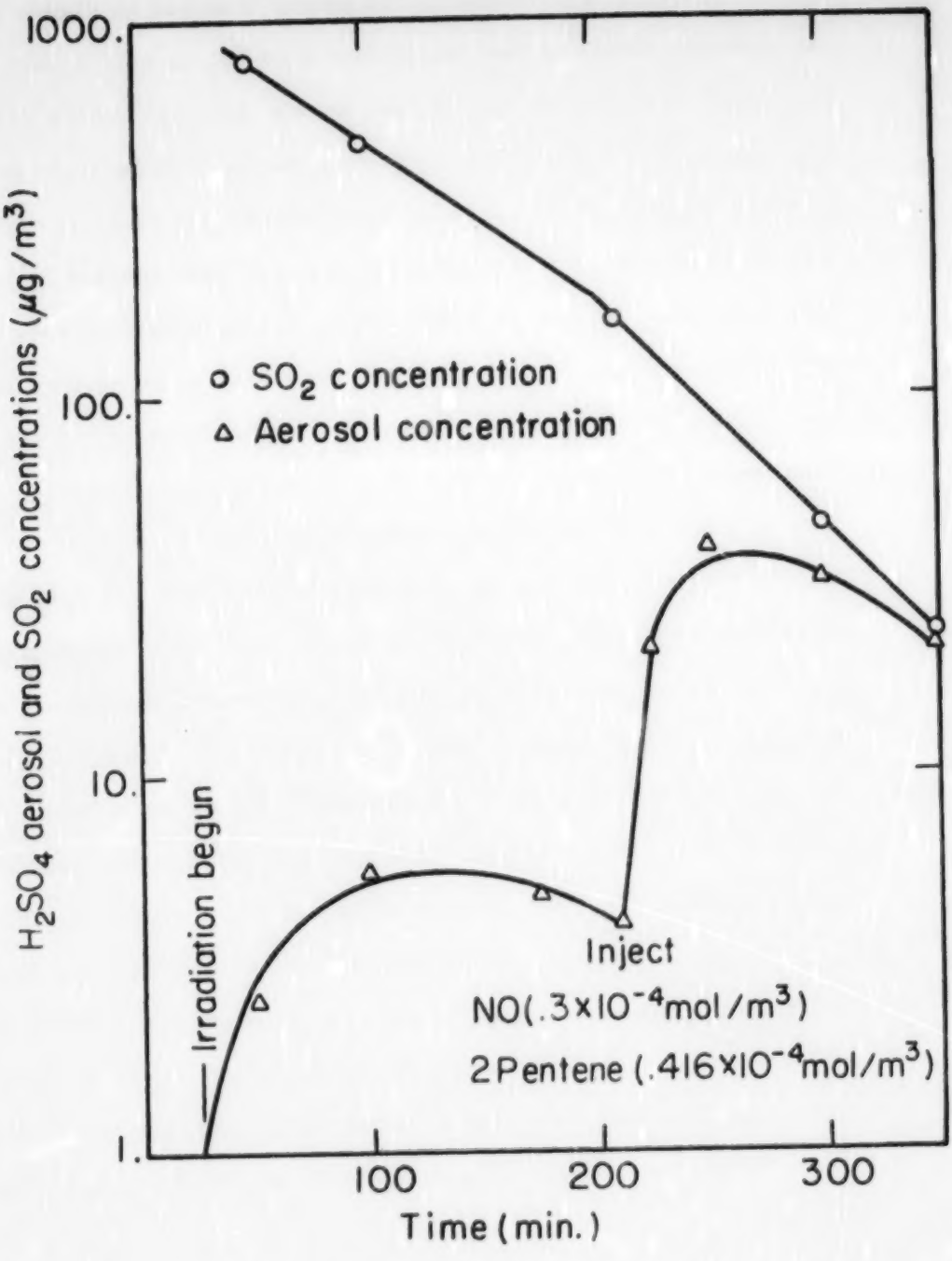

Figure 2. Aerosol formation and SO_2 decay during the photooxidation of SO_2.

where M is a molecule of O_2 or N_2, which acts to carry off excess energy, thereby preventing prompt reversal of this reaction. Mulcahy, Steven, and Ward (1967) found the rate constant for this reaction at room temperature and from 0.7 - 3 torr ($0.9\text{-}4\times10^{-3}$ atm) to average $(2.7\pm0.5) \times 10^{3}$ m^{6} mol^{-2} sec^{-1}. Friend, Leifer and Trichon (1973) calculated the rate of SO_2 removal from the atmosphere by this reaction to proceed quite slowly; 6×10^{-3}% hr^{-1} at sea level and 2.5×10^{-4}% hr^{-1} at 20 km.

Davis, Payne, and Stief (1972) suggested that the reaction of SO_2 with the hydroperoxyl radical might also be of importance in the stratosphere

$$SO_2 + HO_2 \rightarrow SO_3 + OH$$

They found the rate constant for this reaction to equal 1.8 m^{3} mol^{-1} sec^{-1} (± factor of 3). Based on estimated stratospheric HO_2 levels made by Nicolet (1972), Friend et al. (1973) concluded that this reaction would ultimately lead to the production of comparable if not greater amounts of sulfate then would be produced by the reaction of SO_2 with atomic oxygen

Friend et al. (1973) also offer a reaction sequence showing the 3-bodied hydrolysis of SO_3 to H_2SO_4 and the subsequent hydrolysis of the sulfuric acid to H_2SO_4 solutions, or acid embryos. These solutions are neutralized by their reaction with ammonia to form "salt embryos". The salt embryos act as nuclei for growing stratospheric particles on which the oxidation of SO_2 occurs as follows:

$$2SO_2 + 2H_2O + O_2 \xrightarrow[NH_4^+]{\text{embryo}} 2H_2SO_4\text{(solution)}$$

The NH_4^+ acts as a catalyst. When the ammonia is depleted from the surrounding atmosphere, Friend et al. suggest that further absorption and oxidation of SO_2 on the particle will be inhibited due to a drop in pH as the buffer capacity of the NH_4^+ ion is exceeded. This reaction sequence is thought to be responsible for the layer of H_2SO_4 and sulfate particles found in the lower stratosphere.

Perhaps the best way to summarize the possible reactions involving SO_2 in the atmosphere would be by repeating the summary made by Robinson and Robbins (1968). "It seems that in the daytime and at low humidity, photochemical reaction systems involving SO_2, NO_2 and hydrocarbons are of primary importance in the transformation of SO_2 into essentially an H_2SO_4 aerosol. At night and under high humidity or fog conditions, or during actual rain, it seems that a process involving the absorption of SO_2 by alkaline water droplets and a reaction to form $SO_4^=$ within the drop is a well-documented process and can occur at an appreciable rate to remove SO_2 from the atmosphere."

Environmental Sulfur Cycle

Table VII summarizes the estimates made by Eriksson (1960), Junge (1963), Robinson and Robbins (1968), Kellogg et al. (1972) and Friend (1973) in compiling their respective sulfur cycles. It should be kept in mind that while all the values given are only estimates, the degree of uncertainty in some is greater than that in others. For instance, there are no measurements upon which estimates of the quantity of H_2S or $S^=$ emitted by decaying land and sea biota can be based. Also, there are no specifications of the form of sulfide emitted (i.e., H_2S, HS^-, or $S^=$). These estimates have therefore been arrived at by the

Table VII. ATMOSPHERIC FLUXES INVOLVED IN VARIOUS SULFUR CYCLES (in 10^9 kg S per year)

	Eriksson (1960)	Junge (1963)	Robinson and Robbins (1968)	Kellogg et al. (1972)	Friend (1973)
I. Source					
a. anthropogenic, SO_2	40	40	70	50	65
b. natural					
1. volcanoes, SO_2	--	--	--	1.5	2
2. biological decay, H_2S (land)	110	70	68	{90}	58
3. biological decay, $^2S^=$ (oceans)	170	160	30		48
4. sea spray, $SO_4^=$	40	--†	44	43	44
TOTAL	360	270	212	184.5	217
II. Transport {needed to balance the atmosphere internally}					
a. atmospheric transport, SO_2, $SO_4^=$	-10	-30	+26	+5	+8
b. sea spray transport (sea→land)	5	--†	4	4	4
III. Sinks					
a. vegetal absorption, SO_2	75	70	26	15	15
b. oceanic absorption, SO_2	100	70	25	--	25
c. precipitation (land)	{65}	56†	70	86	86
d. dry deposition (land)		15	20	10	20
e. precip. and dry dep., $SO_4^=$ (oceans)	100	60†	71	72	71
TOTAL	340	271	212	183	217
IV. Miscellaneous					
a. fertilizer application	10	{25}	11	--	26
b. rock weathering	15		14	--	42
c. pedosphere → river runoff	55	70	48	--	89
d. total river runoff	80	95	73	--	136

†Junge's model concerned excess sulfur only, therefore effect of sea salt on the cycle was not included.

authors' balancing of particular portions of their cycles; the difference needed to balance each section has then been set equal to the flux of H_2S or $S^=$ from the land and sea to the atmosphere, respectively.

GLOBAL SULFUR CYCLE

A schematic global sulfur cycle is shown in Figure 3. This diagram is a slightly modified version of that devised by Friend (1973). The only modifications other than layout is the addition of atmospheric oxidation schemes for H_2S and SO_2, as well as a flux for the sorption of SO_2 by soils (Eriksson, 1963). The other fluxes shown in this diagram are listed in column 5 of Table VII. All fluxes related to the atmospheric sulfur cycle are discussed separately in the sections concerning the sources and sinks of these compounds. The fluxes between the pedosphere, hydrosphere, and lithosphere have been discussed in detail by Friend (1973). All fluxes are given in Tg S/yr (10^{12} g S/yr).

The sulfur inventory of the various reservoirs or spheres are encircled and given in Tg S. All inventories are as shown by Friend (1973).

From cycles such as this the residence time of sulfur, or the time taken for a complete turnover of the burden in a reservoir, can be calculated for both the atmosphere and hydrosphere. The residence time, τ, of a substance is defined as $\tau = M/R$, where M is the burden or inventory of the substance in a reservoir, and R is the total flux in to or out of that reservoir. The residence time of sulfur in the atmosphere then is equal to

$$\tau = M/R = 1.8 \text{ Tg}/(217 \text{ Tg/yr}) = 0.0083 \text{ yr} = 2.7 \text{ days}$$

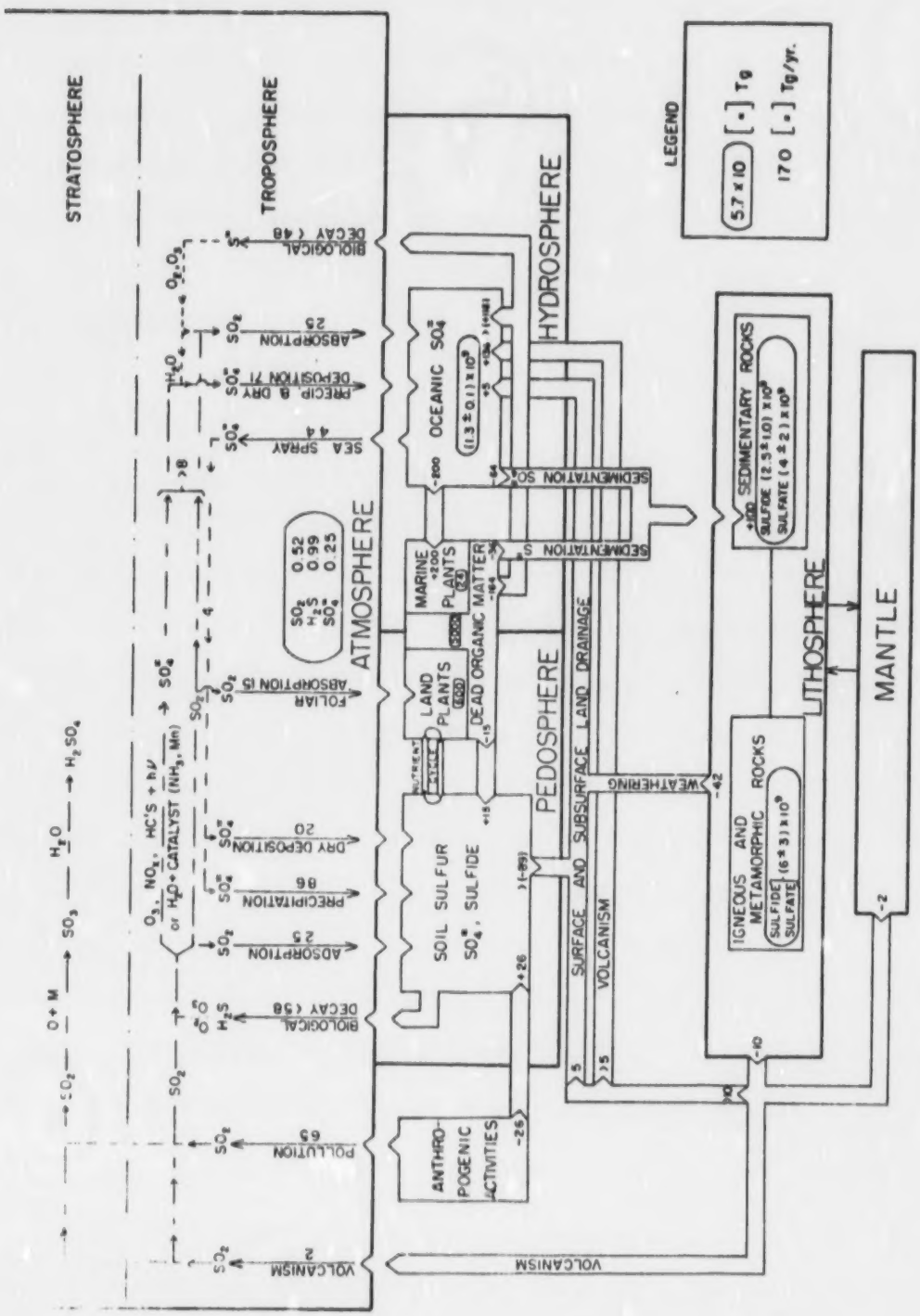

Figure 4. The Global Sulfur Cycle.

(Friend, 1973). The residence time of particular sulfur compounds would be different. Hidy (1973) has calculated the atmospheric residence time of SO_2 to be 4 days and that of H_2S to be 2 days. Nordo (1973) has estimated the residence time of SO_2 to range between 20 minutes and 7 days. Individual estimates of the residence time of sulfate in the atmosphere have not been made, although it is probably comparable to that of sea salts, or about a day or two (Eriksson, 1963).

Using Friend's data a calculation of the residence time of $SO_4^=$ in the oceans can be made as follows:

$$\tau = M/R = \frac{(13\pm0.1) \times 10^8 \text{ Tg}}{3.08 \times 10^2 \text{ Tg/yr}} = (4.22\pm.324) \times 10^6 \text{ years}$$

or about 4 million years. This estimate is a bit under half that of Mackenzie and Garrels (1966). They calculated the residence time of $SO_4^=$ in the oceans to be 10 million years based on river input data. Holser and Kaplan (1966) have calculated the residence time at 21 million years based on their own geochemical cycle. The values they use for the sulfur inventory of the ocean and fluxes out of the ocean are essentially the same as Friend's. However, they do not include an estimate of the sulfur removed by marine plants. As a result, their fluxes are underestimated by about 164 Tg/yr. Even without this flux though, the residence time they calculated was not reproducible. The information given in their cycle leads to a $SO_4^=$ residence time of about 9 million years.

CARBON CONTAINING GASES

CARBON MONOXIDE

Each year more carbon monoxide is released into the atmosphere than any other pollutant (excluding carbon dioxide), and, each year the quantity released increases. One would therefore expect a gradual increase in ambient CO levels, yet one finds that the background concentration of this gas in the atmosphere has not fluctuated the last few decades. There must then be one or several major active sinks for CO within the troposphere. Until just a few years ago though, investigations on possible sinks had only turned up additional sources of CO. This dilemma, as a result, came to be known as the "CO sink anomaly".

Background concentrations of CO range from 47-230 $\mu g/m^3$ (0.04-0.20 ppm) (Jaffe, 1973). Robinson and Robbins (1968) indicate that a mean concentration of 100 $\mu g/m^3$ (0.1 ppm) is found in the northern hemisphere, while concentrations less than 58 $\mu g/m^3$ (0.05 ppm) would probably be more common in the southern hemisphere.

Sources

Carbon monoxide is the product of incomplete combustion of fossil fuels containing carbon. With the advent of large scale industrialization and the tremendous increase in the use of the automobile, great quantities of CO have been emitted into the atmosphere. Recent investigations for CO sinks to explain why the ambient CO concentration has not been increasing have resulted in the discovery of new natural sources of CO whose total quantity far exceeds the total mass of CO produced as a result of man's technology (Stevens et al., 1972).

By far the greatest single anthropogenic source of CO is motor vehicle exhaust. Jaffe (1973) estimated that of a total anthropogenic CO emission source in the United States in 1970 of 132.6 x 10^9 kg, 96.9 x 10^9 kg resulted from the burning of gasoline by motor vehicles alone. Other significant contributions to this man-made CO burden are from solid waste disposal (6.5 x 10^9 kg), industrial process loss (10.3 x 10^9 kg) and agricultural burning (12.5 x 10^9 kg).

Jaffe estimated the total CO emitted by combustion processes on a global scale for 1970 to be approximately 360 x 10^9 kg. He notes that whereas the level of CO produced by man in the United States appears to be leveling off, globally it is on an increase. Underdeveloped nations, which are undergoing increased technological development are not, as yet, concerned with the resulting pollution as much as the economic gains and so their emission levels are on the rise.

The most widely recognized natural source of CO is forest fires which have been estimated as releasing 11 x 10^9 kg CO into the atmosphere each year (Robinson and Robbins, 1968). This is, by no means, the only major natural source of CO. Jaffe (1973) has written an excellent review on all possible natural CO sources. The following is condensed from that paper.

Minor amounts of CO have been found to be released from volcanoes and marshes (Flury and Zernik, 1931). CO can also be formed during electrical storms (White, 1932) and by the photodissociation of CO_2 in the upper atmosphere (Bates and Witherspoon, 1952); Calvert, Kerr, Demerjian and McQuigg, (1972) have suggested the photodissociation of formaldehyde as a possible source of CO and recently, Swinnerton, Lamontagne and Linnenbom (1971) found CO to be present in rain water

in rather high concentrations. Galbally (1972) offered a hypothesis wherein the CO in rain is a product of the photodecomposition of aldehydes in the rain water by sunlight.

The ocean was first suggested as a major source of CO by Swinnerton, Linnenbom and Lamontagne (1970). Linnenbom, Swinnerton and Lamontagne (1973) have estimated the oceans can produce up to 220 x 10^9 kg each year, whereas Liss and Slater (1974) have estimated this flux at 43 x 10^9 kg per year. Robinson and Moser (1971) suggested that plants could indirectly be the source of about 54 x 10^9 kg CO by the oxidation of released terpenes. Finally, McConnell, McElroy and Wofsy (1971) suggested that approximately 900 x 10^9 kg CO are produced each year by the oxidation of methane.

In light of this new source information, Stevens et al. (1972) believe that natural sources of carbon monoxide could yield about 10 times more CO than all anthropogenic sources in the northern hemisphere. Up to this time it has been assumed that anthropogenic activity released far more carbon monoxide than nature. It will be interesting to follow the outcome of this contradiction over the next few years.

Removal Mechanisms

Carbon monoxide can be regarded, for all intents and purposes, as being insoluble in water; its actual solubility being only 0.00234g/100g H_2O at 20°C and 1 atm. Therefore, wet processes such as washout and rainout can be regarded as playing an insignificant part in the removal of CO from the atmosphere. Experiments on the absorption rate of CO by an alfalfa canopy (Hill, 1971) showed that virtually no CO was absorbed and therefore, vegetation can be disregarded as a sink. Absorption of

CO by the oceans can now be disregarded as well because it has recently been shown (Swinnerton et al., 1970) that the oceans actually constitute a significant natural source of carbon monoxide. It seems then that the major sinks for CO are gas-phase reactions in the troposphere and stratosphere and absorption by soil fungi (Inman, Ingersoll and Levy, 1971, and Inman and Ingersoll, 1971).

There are two schools of thought concerning the sources and removal mechanisms of CO in the atmosphere. The old school believed that anthropogenic emissions far surpass natural emissions of CO into the environment, and, due to lack of information at that time, did not recognize that chemical reactions in the stratosphere and troposphere play an important part in destroying CO. Estimates of the residence time of CO in the atmosphere in this school ranged from less than 4 years (Bates and Witherspoon, 1952) to 2.7 years (Robinson and Robbins, 1968). The new school recognizes the importance of natural sources of CO to the tropospheric inventory as well as the importance of both stratospheric and tropospheric reactions in removing it. Residence times estimated by this school are on the order of 0.1-0.2 years (Weinstock, 1969; Levy, 1971; Dimitriades and Whisman, 1971; and Levy, 1973b). In light of the new information available on sources and sinks of CO, it may be unfair to segregate residence time estimates into those arising from old and new schools of thought. For clarification purposes the separation does seem necessary.

Soil: Experiments by Inman and Ingersoll (1971) showed that both potting soils and natural soils absorbed significant amounts of CO. They observed that, in general, soils with the highest uptake activity were

those with higher organic content and lower pH. Inman et al. (1971) also noted that if a soil was autoclaved (sterilized) removal of CO by the soil was inhibited. This suggested that the removal was due to biological activity in the soil. Table VIII (Inman et al., 1971) summarizes the results of tests on several natural soils performed in the laboratory. Further tests isolated some aerobic micro-organisms which were present in the soil and were then tested for their CO uptake abilities. The following fungi were found to be active in removing CO from the soil: 4 strains of Penicillium digitatum, 1 strain of Penicillium restrictum, 4 strains of aspergillus, 1 of Mucor hiemalis, 2 of Haplosporangium parium and 2 of Mortierella vesiculato.

In late 1972 Ingersoll published the results of a more extensive study on the uptake of CO by soils. He measured the in situ uptake at various locations throughout North America. Following is a short summary of his findings.

1) Total amounts of CO destroyed by various soils ranged from 7.5 to 109.0 mg $CO/m^2 \cdot hr$, the spectrum ranging from tropical soils which were the most active down to desert soils which were the least active. Although there were many exceptions, more CO tended to be destroyed by soils with low pH and moderate moisture content ($\sim$20%) than others.

2) The rate of CO uptake decreased as the concentration of CO decreased in the air, with maximum removal with ambient concentrations of 100,000 $\mu g/m^3$ (100 ppm).

3) Given the same soil, CO uptake was far greater when vegetation was growing than when the soil was under cultivation. Ingersoll suggests this is because the amount of organic matter present in soils

Table VIII* RATE OF REMOVAL OF CO FROM TEST ATMOSPHERES AT 25°C BY VARIOUS SOILS

Location of Soil**	Vegetation	pH	Sand: silt:clay (%)	Organic Matter (%)	CO uptake† (mg/hr per square meter of soil)
Eureka-Arcata	Coast redwoods	5.7	53:34:13	25.1	16.99
H. Cowell State Park	Oak	5.3	73:12:15	11.2	15.92
H. Cowell State Park	Coast redwoods	5.7	57:26:17	13.6	14.39
Lake Arrowhead‡	Ponderosa pine	6.2	65:24:11	17.4	13.39
Redding	Grass-legume pasture	5.1	53:32:15	21.0	11.94
Riverside‡	Grapefruits§	6.6	75:14:11	4.3	11.48
Yosemite Valley	Grass meadow	5.05	49:42:9	20.6	10.52
Kauai, Hawaii	Forest	4.74	58:18:24	22.8	9.96
San Bernardino Freeway‡	None	7.2	55:30:15	2.2	6.89
Mojave Desert	Chaparral	7.9	79:6:15	2.4	6.46
Woodland	Oak stubles§	6.6	33:32:35	2.1	6.23
Riverside (desert)‡	Chaparral	7.35	85:4:11	1.0	4.31
Yosemite wall	White fir	5.1	65:18:17	5.7	3.48
Corcoran	Cotton (fallow)§	7.1	57:22:21	2.8	3.48
Hanford	Almond§	6.95	53:26:21	3.5	2.82
Boynton Beach, Florida	Weeds (fallow)§	6.0	86:0:14	1.4	2.65
Oahu, Hawaii		4.93	40:26:34	15.3	2.16

*Table taken directly from Inman et al. (1971). **All soils were collected in California unless otherwise noted. †Average rate at the end of the test period; two to three determinations. ‡Locations where high levels of air pollution occur as a result of the combustion of fossil fuels and photochemical smog. §Land under cultivation or with recent history of cultivation.

being cultivated is substantially lower than that present in soils actively growing crops.

4) Soils that were removed from their site of origin and tested in the laboratory showed greatly reduced uptake ability. The magnitude of decrease was not uniform from one soil sample to the next.

Based upon data he had collected which he corrected for temperature and uptake variations, Ingersoll (1972) estimated the CO uptake potential of the conterminous United States and the world. His estimates of 505×10^9 kg and 14.3×10^{12} kg CO per year for each, respectively, are based on ambient CO levels of 100,000 $\mu g/m^3$ (100 ppm), three orders of magnitude greater than average ambient CO levels. Ingersoll noted though that Seiler (1972) had found soil CO uptake rates to be one-tenth of those Ingersoll had measured when these soils were exposed to ambient CO levels (230-1200 $\mu g/m^3$) rather than concentrations of 100,000 $\mu g/m^3$. On the basis of this information, Ingersoll reduced his estimates of the total capacity of soils to consume CO in the United States and the world to around 50×10^9 kg and 1.4×10^{12} kg per year, respectively. Because Seiler's article has not been published, it is impossible to state whether his uptake measurements were taken in the field or the laboratory. Ingersoll, as mentioned above, has found that uptake rates for the same soil were greatly reduced when taken in the laboratory as compared to field measurements. Unless measurements were taken by both Ingersoll and Seiler under the same conditions, one must question the validity in using Seiler's data to reevaluate estimates made using Ingersoll's data. Since the estimates made at this stage are only a first approximation, perhaps such concerns are unimportant. Earlier, Inman and

Ingersoll (1971) also estimated that soils of the continental United States were capable of removing over 500 x 10^9 kg CO per year.

Based on measurements of the CO uptake rate of two soils, Heichel (1973) concluded that the resistance of the soil to CO removal increases as the moisture content of the soil decreases, and also increases as the degree of air circulation above the soil decreases. Comparing his uptake and resistance measurements with those of Turner, Rich and Waggoner (1973) who measured the uptake rate of ozone on one of the same soils, Heichel found the rate of CO removal by the soil to be 2-3 orders of magnitude less than the removal of O_3. There was also a correspondingly greater resistance to removal of CO than O_3. Heichel determined on the basis of his measurements, and assuming an average ambient CO level of 350 $\mu g/m^3$ (0.3 ppm), that the land can remove the equivalent of 14% of the tropospheric CO inventory of 4.75 x 10^{11} kg CO (Weinstock and Niki, 1972) each year, or about 67 x 10^9 kg/yr.

Recent experiments by Smith et al. (1973) also showed that soils are capable of effectively removing CO from the atmosphere. They also found though that when moist soils were placed in the chamber with air containing 100,000 μg CO/m^3 (100 ppm), the concentration of CO in the chamber rose, in one case tripled, before it was reduced to zero. This effect was found to be more pronounced in sterilized soils than unsterilized soils. They surmised that the evolution of CO from the soils is a nonbiological process, but made no attempts to identify the processes responsible. Seiler and Junge (1970) also noticed this effect. Their test results showed that at ambient CO levels (200 $\mu g/m^3$, or 0.2 ppm) the rate of CO production by the soil is balanced by the rate of CO

absorption by the soil. This finding lends another complication to the identification of sources and sinks for CO. Perhaps ultimately it will be shown that soils do constitute a major sink for carbon monoxide; first we need to know if there is evidence of CO evolution from in situ soils or whether this is a phenomenon only found in laboratory experiments, and we need quantitative data to see what the ratio of CO evolved to CO removed from the atmosphere is at different ambient CO levels.

Atmospheric Reactions Involving CO: Recently it has become apparent that the stratosphere constitutes a sink for carbon monoxide. The significant reaction seems to be the reaction of CO with the hydroxyl radical (Weinstock, 1969; Pressman and Warneck, 1970; and Pressman et al., 1970) as follows:

$$OH + CO \rightarrow CO_2 + H \qquad (1)$$

The rate constant for this reaction at -56°C, the temperature of the lower stratosphere is $k_1 = 6.02 \times 10^4$ $m^3/mol \cdot sec$ (Schofield, 1967). Westenberg (1972) found that the rate constant increases to 10.2×10^4 $m^3/mol \cdot sec$ at room temperature (27°C). Reaction 1 is followed by the sequence:

$$H + O_2 + M \rightarrow HO_2 + M \qquad (2)$$

$$CO + HO_2 \rightarrow CO_2 + OH \qquad (3)$$

The rate constant for reaction 2 has been found to be equal to 4.35×10^{27} $m^6/mol^2 \cdot sec$ (Westenberg and de Haas, 1972).

The significance of reaction 3 has recently been the subject of much debate and experimental work. It was previously believed that the regeneration of the OH radical proceeded via the reaction

$$H + HO_2 \rightarrow 2\ OH \qquad (4)$$

Davis et al. (1973) have concluded that reaction 3 proceeds quite slowly (k_3 probably being less than 6×10^3 m^3/mol·sec) and therefore, should not play a significant role in atmospheric chemistry. Westenberg though believes that reaction 3 probably proceeds even faster than reaction 1. Westenberg and de Haas (1972) derived a rate constant for reaction 3 at room temperature of about 6.02×10^5 m^3/mol·sec which is indeed faster than that of reaction 1. Explanations offered to explain the difference in these k_3 values (Davis, Payne and Stief, 1973) are not conclusive. It has been pointed out (K. L. Demerjian, 1974) that the rate constants for reaction 3 are erroneous. For further discussion of these reactions and many more of interest the reader is referred to a recent work by Demerjian (1973).

Naturally, if this mechanism is correct it would require that a significant amount of hydroxyl radicals be present. Assuming that CO is in a steady-state in the atmosphere with a concentration of 100 $\mu g/m^3$ (.1 ppm) Weinstock (1969) calculated the OH required to maintain this steady state condition according to the equation:

$$[OH] = P/k[CO]$$

where P = production rate of CO and k is the second order rate constant. He calculated that 1.16×10^{-3} mol OH/m^3 were required and that requirement could easily be satisfied by an OH regenerative process as suggested above.

Vertical CO profiles of the atmosphere have recently been measured by Seiler and Junge (1969), Seiler and Warneck (1972) and Goldman, Murcray, Murcray, Williams, Brooks and Bradford (1973). These first two reports both found a sharp decrease in the CO mixing ratio when crossing the tropopause into the stratosphere. The mixing ratio is defined as the mass of gas per unit mass of dry air. Goldman et al's. profile did not show a sharp decrease in the mixing ratio at the tropopause but they believe this might be due to local atmospheric conditions just around Holloman, New Mexico, where their measurements were taken. It seems obvious from vertical profiles such as these that there is a significant decrease in CO levels above the tropopause, thus supporting the conclusion that the stratosphere is a sink for carbon monoxide.

Quantitative estimates of the CO destroyed in the stratosphere by this reaction mechanism have not been made, although Pressman and Warneck (1970) believe that virtually all CO entering the stratosphere is so destroyed. Therefore, the size of the stratospheric sink is dependent upon the transport rate of CO rich air through the tropopause into the stratosphere. They have estimated this flux at 1.3×10^{-3} $mol/m^2 \cdot sec$ but admit the degree of uncertainty in this estimate is very high due to insufficient data. Based on this flux and recent estimates of the total CO reservoir in the troposphere, they estimated that about 11-15% of the total CO inventory in the troposphere is destroyed in the stratosphere by the reaction sequence mentioned above, or about $52\text{-}71 \times 10^9$ kg/yr.

Although the above reaction sequence has been recognized as a major sink in the stratosphere, only recently has it been suggested to be a

significant destructive reaction in the troposphere (Weinstock, 1969). Recent investigations (Levy, 1971; McConnell, McElroy and Wofsy, 1971) have shown that sufficient amounts of hydroxyl and hydroperoxyl radicals exist in the troposphere to provide a mechanism for CO oxidation there as well.

Levy (1971) suggested the following reaction sequence which provides for both the production of hydroxyl and hydroperoxyl radicals and the oxidation of CO and NO in the troposphere.

(1) $O_3 + h\nu \ (2900\text{Å} < \lambda < 3400\text{Å}) \rightarrow O(^1D) + O_2$

(2) $O(^1D) + M \rightarrow O(^3P) + M$

$$k_2 = 3.01 \times 10^7 \ m^3 \ mol^{-1} \ sec^{-1}$$

(3) $O(^1D) + H_2O \rightarrow 2OH$

$$k_3 = 1.8 \times 10^7 \ m^3 \ mol^{-1} \ sec^{-1}$$

(4) $OH + O_3 \rightarrow HO_2 + O_2$

$$k_4 \leq 3.01 \times 10^5 \ m^3 \ mol^{-1} \ sec^{-1}$$

(5) $OH + CO \rightarrow CO_2 + H$

$$k_5 = 9.0 \times 10^4 \ m^3 \ mol^{-1} \ sec^{-1}$$

(6) $H + O_2 + M \rightarrow HO_2 + M$

$$k_6 = 1.08 \times 10^4 \ m^6 \ mol^{-2} \ sec^{-1}$$

(7) $HO_2 + NO \rightarrow NO_2 + OH$

$$k_7 = 3.01 \times 10^5 \ m^3 \ mol^{-1} \ sec^{-1}$$

More recent estimates of these rate constants by Kummler and Bauer (1973) are in excellent agreement with those of Levy listed above.

Although quantitative estimates of the total CO possibly consumed by this reaction series have not been made, Levy did calculate a carbon monoxide lifetime in the surface atmosphere of 0.2 years using hydroxyl radical concentrations which he had determined. This estimate is in good agreement with that made by Dimitriades and Whisman (1971), but is still the subject of considerable dispute among other scientists (Kummler, Bortner and Jaffe, 1971) who produce their own evidence to show that gas phase kinetics at ground level cannot alone explain the sink anomaly.

Carbon Monoxide Cycle

The last several years have seen an explosion of interest in defining natural CO sources and sinks. While several researchers have confirmed that soil and the reaction of CO with hydroxyl and hydroperoxyl radicals in the stratosphere and possibly the troposphere constitute a major sink for CO, other researchers have found additional natural sources of this gas. These sources, which include oxidation of methane, oxidation of terpenes and the oceans to name just a few, are now thought to contribute more CO to the atmosphere than that emitted from anthropogenic activity. This is an outright contradiction of what only two years ago was thought to be the final word; i.e., anthropogenic CO emissions are many times greater than natural CO emissions.

Table IX compares recent estimates of the importance of CO sources and sinks. It is obvious from this table, if these estimates are at all reasonable, that soil and gas-phase oxidation in the stratosphere and troposphere might be capable of consuming all the CO that nature and man produce. If so, this explains why the background concentration of CO has not increased over the last several decades, and we might suggest that there no longer exists a "CO sink anomaly".

Table IX. ATMOSPHERIC FLUXES OF CARBON MONOXIDE (in 10^9 kg/yr)

I. Sources		
a. anthropogenic	359	Jaffe (1973)
b. natural		
1. oceans	43-220	Liss and Slater (1974)-Linnenbom et al. (1973)
2. oxidation of terpenes	54	Robinson and Moser (1971)
3. oxidation of methane	900	McConnell et al. (1971)
4. other	?	
TOTAL	1356-1533	
II. Sinks		
a. soil	67-1400	Heichel (1973)-Ingersoll (1972)
b. gas-phase oxidation		
1. stratosphere	52-71	Pressman and Warneck (1970)
2. troposphere	?	
TOTAL	119-1471	

NITROGEN CONTAINING GASES

Although the most abundant oxide of nitrogen in the lower atmosphere is nitrous oxide (N_2O), it does not play an important part in air pollution chemistry. The two nitrogen oxides which are important are nitric oxide (NO) and nitrogen dioxide (NO_2) for they play a prominent role in the generation of photochemical smog. In fact, the presence of nitrogen dioxide, as a light energy acceptor, is a necessary condition for photochemical reactions to proceed.

Measurements of the background levels of nitrous oxide consistently average to about 460-490 $\mu g/m^3$ (0.25-0.27 ppm) (Schütz, Junge, Breck and Albrecht, 1970). Ambient NO_2 levels are much lower, probably around 2 $\mu g/m^3$ (.001 ppm) (Robinson and Robbins, 1968) to 2.6 $\mu g/m^3$ (.014 ppm) (Junge, 1963). Too few accurate measurements have been made of ambient levels to obtain a meaningful average, but Lodge and Pate (1966) found concentrations up to 11 $\mu g/m^3$ (.006 ppm) in Panama. Not many measurements of NO levels have been made but they are approximately the same as those of NO_2.

The other nitrogen compound considered is ammonia. Although ammonia, per se, is a relatively unimportant air pollutant, it does play an important role in atmospheric chemistry through its part in the formation of aerosols. Ambient concentrations of ammonia seem to average about 4 $\mu g/m^3$ (.006 ppm) (Robinson and Robbins, 1968).

NITROGEN OXIDES

Sources

Nitrous oxide (N_2O), the most abundant nitrogen compound in the atmosphere, is produced from bacterial decomposition of other nitrogen compounds within the soil. Arnold (1954) was the first to study the production of N_2O by soils. He found that the factor most conducive to increased N_2O evolution is a high soil moisture content, especially if a nitrogen source, such as nitrate or ammonia, is present. Bacterial decay is the primary source of nitrous oxide and so is probably responsible for ambient N_2O concentrations. An estimate of the flux of N_2O from soils into the atmosphere has recently been made by McConnell (1973). He estimates that although an unknown amount is released and reabsorbed, about 1.1×10^{10} kg N_2O - N (1.73×10^{10} kg N_2O) are available for oxidation or photolysis to NO_x and N_2 in the stratosphere each year. Schütz et al. (1970) declined to extrapolate the data they collected on three soil samples to attain a global flux. Their measurements showed a flux on the order of 10^{-8} g $N_2O/m^2 \cdot sec$, an order of magnitude which, if maintained globally, would necessitate an N_2O residence time of about 70 years. This is the same residence time they estimated based on the photodissociation rates of N_2O in the troposphere and stratosphere. Goody and Walshaw (1953) estimated a global N_2O production rate of about 100×10^{12} kg/year and Robinson and Robbins (1968) suggested that soils produce about 59.2×10^{10} kg N_2O each year by biological action; and of this about 55.4×10^{10} kg (35.3×10^{10} kg N_2O - N) are reabsorbed by the soil and about 3.8×10^{10} kg N_2O (2.4×10^{10} kg N_2O - N) travels up to the stratosphere where it is destroyed. It is this latter rate that is shown in Table XI.

Craig and Gordon (1963) raised the possibility that the ocean might be a source or a sink of N_2O. Bates and Hays (1967) concluded though that the uptake of N_2O by the oceans in areas where upwelling waters are deficient in N_2O is of negligible importance. Based upon the difference between the mean N_2O concentrations of oceanic surface waters and adjacent air, and an estimate of the total liquid phase resistance, Liss and Slater (1974) estimated the flux of N_2O from the ocean to the atmosphere at 1.2×10^{11} kg/year. This flux is based entirely on theory, but indicates that the oceans could conceivably release significant quantities of N_2O to the atmosphere. Laboratory and field experiments are needed to decide whether or not the ocean is a source of N_2O.

Production rates of NO and NO_2 by soils are much more difficult to measure or estimate, and good data are lacking. McConnell (1973) recently summarized a few of the problems involved in appraising the amount of nitrogen oxides produced by soil. He contends that this soil source is small compared to that produced as a result of the gas phase oxidation of atmospheric ammonia by OH which he thinks produces 7×10^{10} kg NO_x - N per year. McConnell offers alternative reaction sequences for NH_3 in the atmosphere; one reaction sequence provides a constant source of NO, the other a sink. If the latter is shown to occur in the atmosphere, in order to account for the amount of NO known to be in the atmosphere, then an additional source of NO must be found. In this case, McConnell concedes that the soil might actually constitute a significant source of NO_x, on the order of 10^{11} kg/yr.

Nitric oxide is also produced as a result of the photolysis of N_2O in the stratosphere as follows:

$$N_2O + h\nu \rightarrow NO + N$$

The photolysis rate for this reaction is less than or equal to 7.4×10^{-9} sec^{-1} (McElroy and McConnell, 1971). Whereas these authors estimate the production of about 3×10^8 kg NO_x - N per year in this manner, Bates and Hays (1967) estimated that 3.5×10^{10} kg NO are produced annually by this photolysis reaction.

The other primary source of nitrogen oxides is anthropogenic, primarily combustion processes. Estimates of production rates for NO and NO_2 are included together because available emission data rarely distinguish between these two forms. Robinson and Robbins (1970) estimated that 53×10^9 kg of NO_2, or 16×10^9 kg NO_2 - N were emitted annually (here again NO_2 includes both NO and NO_2 production).

In toto, natural emissions of NO_2 (including NO) are approximately 15 times greater than anthropogenic emissions (768×10^9 kg vs. 53×10^9 kg NO_2) (Robinson and Robbins, 1970). Therefore, anthropogenic emissions play only a minor part in the total circulation of nitrogen compounds in the atmosphere.

Removal Mechanisms

At 20°C and 1 atm total pressure, the solubility of N_2O in water is 0.12i g/100g H_2O. Upon release from soils, an unknown portion is believed to be removed by vegetation, soil and water. No information is available on these reactions. The major portion of the released N_2O is destroyed by photodissociation in the stratosphere and upper troposphere. Under normal tropospheric conditions, N_2O is chemically inert and it partakes in no other chemical reactions. The resid ce time of

nitrous oxide is probably around 70 years if there is no removal by the biosphere (Robinson and Robbins, 1968), but could be reduced to about 1-3 years if there is a biologic loss mechanism. Hidy (1973) estimated the residence time as 4 years.

Nitric oxide is rather insoluble in water. At 20°C and 1 atm total pressure, its solubility is 0.00618 g/100g H_2O. Nitrogen dioxide, on the other hand, immediately dissociates in water to form HNO_3 and HNO_2. For this reason the solubility of NO_2 in water is practically unlimited.

Nitric oxide is either oxidized to NO_2 or photolyzed to N_2. The NO_2 is then removed primarily be precipitation, more often than not in the form of nitric acid (HNO_3). It can also be absorbed by vegetation and soils or participate in photochemical reactions to form aerosols. Due to their reactivity, the residence timesof NO and $NO_2$are relatively short, probably around 5 days (Hidy, 1973). Nitrogen oxides are removed from the atmosphere by the following mechanisms.

Vegetation: Vegetation has been shown capable of removing significant amounts of NO_2 and NO from the atmosphere. Tingey (1968) showed that alfalfa and oats absorbed NO_2 from the air in excess of 100×10^{-12} $mol/m^2 \cdot sec$ when exposed to an atmosphere containing 460 µg NO_2/m^3 (or $\sim 1 \times 10^{-5}$ mol/m^3). With time, the uptake rate of NO_2 by plants exposed to air containing between 300 and 460 µg NO_2/m^3 decreased, whereas the uptake rate remained constant when the plants were exposed to only 150 µg NO_2/m^3. He also found that there was no decrease in absorption rates when the intensity of the sunlight was reduced.

Tingey extrapolated his data to estimate the removal of NO_2 from the Salt Lake Valley in Utah. His estimates, based on an areal extent

of about 2000 km^2 in the valley with an 85% vegetal covering in the summer, are tabulated below (Table X).

Table X. RATES OF NO_2 UPTAKE IN SALT LAKE VALLEY, UTAH

NO_2 Conc. (24-hr average)	Removal Rate per km^2 (kg/day)	Removal Rate from Valley (kg/day)
40 $\mu g/m^3$	18	36×10^3
20 $\mu g/m^3$	9	18×10^3
10 $\mu g/m^3$	4.5	9×10^3

On an annual basis, removal of NO_2 from the valley with an ambient NO_2 concentration of 9.6 $\mu g/m^3$ (about 3-4 times greater than background NO_2 levels) would total about 3×10^6 kg NO_2. This may be compared with the estimated total global anthropogenic annual NO_2 emissions of 53×10^9 kg (Robinson and Robbins, 1970).

Hill (1971) found in his experiments on the uptake rate of gases by an alfalfa canopy that NO was absorbed with a depositional velocity of 0.1 cm/sec. NO_2 was absorbed at a velocity of 2 cm/sec when present in the air of the chamber at a concentration of 2×10^{-6} mol/m^3 (or 96 $\mu g/m^3$). Using ambient NO_2 concentrations found in those areas of Southern California from August to October of 1968, and assuming a continuous alfalfa cover, Hill estimated that NO_2 could be removed at a rate of 0.1 $g/m^2 \cdot day$. Because nitrogen is often a limiting factor in

plant growth, Hill believes his study shows that NO_2 and NO could supply as much as .03 g $N/m^2 \cdot day$. Since NO_2 dissociates in water, it is expected that the N absorbed from the atmosphere as NO_2 would be metabolized and so the amount absorbed over one year could be significant.

Soil: Nitrogen oxides (especially N_2O) have long been known to be produced by biological action in soils. Recently though, Abeles et al. (1971) found that soils could absorb nitrogen dioxide from the atmosphere as well. They found that when they passed air containing NO_2 over soil in a test chamber, the concentration of NO_2 in the air was reduced from an initial value of 190×10^3 $\mu g/m^3$ (100 ppm) down to 5.7×10^3 $\mu g/m^3$ (3 ppm) over a 24 hour period. When the soil was autoclaved, the total NO_2 present over the same time period was reduced from 186×10^3 $\mu g/m^3$ (97 ppm) to only 25×10^3 $\mu g/m^3$ (13 ppm). The reaction believed to be the cause of the NO_2 uptake in the soil was not discovered. Extrapolating the results of this experiment, the authors suggest that the soils of the United States might be capable of removing 60×10^{10} kg of NO_2 per year from the atmosphere, an amount they point out to be a bit under 20 times the total annual production of NO_2 in this country (3.3×10^{10} kg). Of course, such a removal rate is largely conjectural for there are too many variables that need to be taken into consideration, such as soil moisture content, soil composition, both mineralogical and organic, and vegetal covering to name just a few. Although attempting such an estimate is warranted, the limitations placed upon this value must be kept in mind until more information becomes available.

Nelson and Bremner (1970) point out that the NO_2 absorbed by soil will ultimately be oxidized to nitrate. These nitrates eventually

decompose and result in the production of nitrogen dioxide again. The rate of NO_2 production by nitrate breakdown in soils is 2×10^{-4} g NO_2/ $m^2 \cdot hr$ (Marchesani, Towers, and Wohlers, 1970, and Makarov, 1970, as cited in Bohn, 1972). This NO_2 production rate is dependent upon the nitrate content of the soil and does not proceed during darkness.

Nitric oxide may also be absorbed by soils, but is then oxidized almost immediately to NO_2 (Mortland, 1965; and Bremner and Nelson, 1968). Mortland has also discovered that transition metal ions in the soil promote NO absorption. If the soil is saturated with alkaline earth cations though, absorption of NO is halted. Sundareson, Harding, May, and Henrickson (1967) found that alkaline-earth zeolites readily absorb NO and release it as NO_x and HNO_3 when heated. To date, the role organic matter plays in the absorption of nitrogen oxides by soil remains a mystery. Ganz, Kuznetsov, Shlifer, and Leiken (1968, as cited in Bohn) found that upon passing NO_x-contaminated air through 1 meter of peat, all nitrogen components were removed. Organic matter is such an important component of soil that to not be fully aware of its effects on a gas could only hinder understanding of the mechanism of absorption by the soil. Obviously, more research is needed in this area.

Water Bodies: There are very little data available on the amount of nitrogen oxides absorbed by the oceans. Craig and Gordon (1963) first suggested that the oceans might constitute a sink for N_2O when they found that the sea water at depth was depleted in N_2O compared to the surface waters which they found to be in equilibrium with atmospheric concentrations. This depletion could not be explained by temperature variations with depth. Based on the mean upwelling speed of the ocean's waters,

thought by Bowden (1965) to range from 10^{-4} to 10^{-5} cm/sec, Bates and Hayes (1967) estimated the potential sink strength of the oceans for N_2O as ranging between 6×10^{-7} and 6×10^{-6} kg/m^2·yr. . Liss and Slater (1974), on the other hand, concluded that the flux of N_2O was from the sea to the air. They calculated a flux rate of 3.2×10^{6} kg/m^2·yr based upon an N_2O concentration gradient across the air-sea interface measured by Junge and Hahn (1971). The total flux of N_2O from the sea to the atmosphere, if assumed constant over the entire oceanic surface, is 1.2×10^{11} kg/yr. With such an obvious contradiction as to the direction of the N_2O flux, there is a real need for additional research in this area.

Washout and Rainout: The major sink identified thus far for nitrogen oxides (NO_x) is the solution of soluble species in cloud and rain droplets with subsequent removal by precipitation. According to Haagen-Smit and Wayne (1968) the reaction is:

$$4NO + 2H_2O + O_2 \rightarrow 4HNO_3$$

Georgii (1963) believes the reaction proceeds as follows:

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

Georgii found when a total volume of 20 m^3 of atmospheric air containing average concentrations of NO_2, but cleansed of all natural aerosol particles, was passed over both distilled and rain water at a velocity of 5-10 cm/sec, that the nitrate (NO_3^-) concentration in the rain water increased from 0.18 to 0.45 mg/l while the nitrite (NO_2^-) concentration increased from 0.04 to 0.08 mg/l. Georgii further showed that the NO_3^- concentration in rain is related to the concentration of NO_2 in

the atmosphere. In Frankfurt am Main, Germany, where ambient NO_2 levels are higher in winter than summer, Georgii found that the nitrate content in rainwater was also greater in winter than summer.

Robinson and Robbins (1968) suggested that the dissolution of NO_2 proceeds as follows:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

However the hydrolysis reaction proceeds, the outcome is the same in all cases; the nitric acid formed is absorbed onto hygroscopic particles or reacts with atmospheric ammonia to form nitrate salt aerosols (NH_4NO_3 for instance). It is then either removed by precipitation, or if vaporization of the droplet occurs, by dry deposition.

McConnell (1973) estimates that 2×10^{10} kg NO_3^- - N is removed from the atmosphere each year by precipitation, and an additional 7×10^{10} kg NO_X - N removed by dry deposition, the major portion of this probably being HNO_3.

Atmospheric Reactions Involving Nitrogen Oxides: Although more nitrous oxide is released to the atmosphere than any other nitrogen oxide it does not play a major or very complex role in atmospheric reactions. Because it is chemically inert in the troposphere, its sink lies in the stratosphere where it is transported by vertical mixing and destroyed by photolyzing reactions. Bates and Hays (1967) indicate that the most significant reactions are:

$$N_2O + h\nu \rightarrow N_2 + O\ (^1D)\ ;\ \lambda < 3370\ \text{Å}$$

$$N_2O + h\nu \rightarrow NO + N\ (^4S)\ ;\ \lambda < 2500\ \text{Å}$$

The latter reaction they consider responsible for about 20% of the total dissociation in the stratosphere. They calculate an average latitudinal dissociation rate of about 3×10^{-9} sec^{-1}.

Nitric oxide can be removed from the atmosphere by several reactions. The primary reaction is its oxidation by ozone to form NO_2

$$NO + O_3 \rightarrow NO_2 + O_2$$

which has a rate constant of $9.0 \times 10^{-18} \exp(-1200/T)$ m^3 sec^{-1} (Schofield, 1967). In the upper atmosphere, NO can be photolyzed to atomic N which may react with other NO molecules to form N_2 as follows:

$NO + h\nu \rightarrow N\ (^4S) + O\ (^3P)$; photolysis rate = 4.0×10^{-6} sec^{-1} (Callear and Pilling, 1970)

$N + NO \rightarrow N_2 + O$; $k = 2.2 \times 10^{-11}$ cm^3 sec^{-1} (Schofield, 1967)

Nitrogen dioxide also can engage in a number of reactions. It may be oxidized to gaseous NO_3 by the reaction

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

The rate constant equals $9.0 \times 10^{-18} \exp(-3500/T)$ m^3/sec (Schofield, 1967). Or, it may form nitric acid by its reaction with hydroxyl radicals as follows:

$$OH + NO_2 \rightleftarrows HONO_2^* \xrightarrow{M} HNO_3$$

The nitric acid formed is removed by precipitation. For further elaboration, the reader is referred to McConnell and McElroy's (1973) article.

The importance of NO and NO_2 as pollutants reflect their participation in photochemical reactions. In polluted atmospheres they react with SO_2

and hydrocarbons to form aerosols. Probably the most important photochemical reaction involving NO_2 is its photodissociation as follows:

$$NO_2 + h\nu \ (2900\ \mathring{A} < \lambda < 3800\ \mathring{A}) \rightleftarrows NO + O$$

This atomic oxygen then is free to react with molecular oxygen and form ozone.

Peroxyl radicals (ROO•), formed between reactive free radicals ($\dot{R}$) and O_2, can react with NO and NO_2 to form alkyl nitrates or peroxyacyl nitrates as follows:

$$ROO\bullet + NO \rightarrow ROONO \overset{h\nu}{\rightarrow} RO\bullet + NO_2$$

$$ROO\bullet + NO_2 \rightarrow ROONO_2$$

These secondary reaction products are targets of further photochemical attack. For example, peroxyacyl nitrate may be photodecomposed into NO_2 and acylate radical as follows:

$$RC(=O)\text{-}OONO \overset{h\nu}{\rightarrow} RCO\bullet + NO_2$$

This rather brief overview of possible photochemical reactions involving nitrogen oxides is abridged from Haagen-Smit and Wayne (1968). It is inappropriate here to elaborate on photochemical reactions involving nitrogen oxides. The reader is referred to Altshuller and Bufalini (1971), Cadle and Allen (1970), and Leighton (1961) for more detail.

Environmental NO_x Cycle

The circulation of nitrogen oxides in the atmosphere is complex and not well understood. The global NO_x cycles formulated by Robinson

and Robbins (1968, 1970) and McConnell (1973) make clear how very little good quantitative data exists. A more complete global nitrogen cycle (Figure 4) for both nitrogen oxides and ammonia is presented at the end of the following section on ammonia.

The holes in these cycles are obvious and major ones (see Table XI). We need, for instance, a better idea of how much NO and NO_2 is released from the soil, how much NH_3 is oxidized to NO_x, and how much NO and NO_2 is destroyed by photochemical reactions. We also need to know why large discrepancies exist between estimates, and the bases for these estimates. For example, McConnell bases his estimate of NO_x removed by dry deposition on soil data, the nitrogen content of precipitation and a deposition velocity factor. Robinson and Robbins, on the other hand, use the deposition velocity function to estimate gaseous deposition, a removal mechanism McConnell makes no mention of. These and other inconsistencies indicate the need for further study.

Table XI. ATMOSPHERIC FLUXES INVOLVED IN VARIOUS NO_x CYCLES (10^{10} kg N/yr)

	Robinson and Robbins (1968)	Robinson and Robbins (1970)	McConnell (1973)
I. Sources			
a. anthropogenic; NO, NO_2	1.5	1.6	1.8
b. biological; N_2O	1.2	1.2	1.1
c. biological; NO, NO_2	30.4	23.4	?
d. oxidation of NH_3	N.E.	N.E.	7
e. stratospheric transport; NO, NO_2	---	---	0.07
TOTAL	33.1	26.2	9.97
II. Sinks			
a. rainout	112.9	7.5	2
b. dry deposition	27.1	1.9	7
c. oxidation of $N_2O \rightarrow NO$ (strat.)	0.2	0.2	0.03
d. photolysis of $N_2O \rightarrow N_2$ (strat.)	---	---	(1.07)
e. gaseous deposition	10.7	4.5	---
TOTAL	150.9	14.1	(10.1)

N.E. = Mechanism recognized but no estimate made.

*NOTE: Friend (1973) has pointed out that due to an error in converting units of kilograms per hectare to tons per square meter, much of Robinson and Robbins' nitrogen compound cycle is invalid. Friend though, gives no indication as to which values are wrong. Due to lack of information, their cycle is nonetheless shown for comparison.

AMMONIA

Sources

Most ammonia in the atmosphere is the result of the bacterial decomposition of organic material on the earth's surface. The factors which affect the emission of this NH_3 from the soil are its nitrogen content, pH, and moisture content (McConnell, 1973; and Georgii, 1963). NH_3 is more readily released from dry soils than moist ones, and is more readily released when the pH of the soil is greater than or equal to 6. It has been suggested that in acid soils NH_4^+ is probably biologically oxidized (autotrophic nitrification) to NO_3^- and therefore not available for release. The net oxidation reaction would be

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$$

(Keeney, 1973). DuPlessis and Kroontje (1964), on the other hand, suggested that the low hydroxyl ion activity in acid soils and adsorption of NH_4^+ on soil colloids prevents or retards the release of NH_3, according to the reaction

$$NH_4^+ + OH^- \rightleftarrows NH_3 + H_2O$$

In alkaline soils the activity of OH^- is greater than that of H^+ and so NH_3 is readily released.

Junge (1963) suggested that the oceans may contribute some NH_3 to the atmosphere, but to date there has been no accurate measurement made upon which to base an estimate of the source strength. McConnell has estimated that these biological sources release about 17×10^{10} kg NH_3 - N each year, whereas Robinson and Robbins'(1968) nitrogen cycle calls

for the release of NH_3 on the order of 10^{12} kg NH_3 each year (see Table XV).

Anthropogenic NH_3 emissions result primarily from the combustion of coal. Robinson and Robbins (1970) estimated that the atmospheric ammonia burden due to man's activities is 0.4×10^{10} kg NH_3 - N per year, less than 2 1/2% of the estimated NH_3 burden due to biological emissions (17×10^{10} kg).

Removal Mechanisms

Ammonia is extremely soluble in water. At 20°C and 1 atm its solubility in water is 62.9 g/100g H_2O. Ammonia therefore can be readily absorbed by water bodies and vegetation. It is also removed by its reaction with hydroxyl radicals to form nitric oxide. Probably the most important removal mechanism though is its solution in rain water along with SO_2 or other gases to form aerosols such as $(NH_4)_2SO_4$. The quantity of NH_3 removed by precipitation is ordinarily determined by measuring the quantity of NH_4^+ present in rain. From the data available, the residence time of ammonia in the atmosphere is probably around 7 days. The following mechanisms are important in removing ammonia from the atmosphere.

Vegetation: Because it is normally present in the atmosphere in such small concentrations, ammonia's interaction with soil, water and plants has long been ignored. Hutchinson, Millington and Peters (1972) and Porter, Viets and Hutchinson (1972) have found that even at the low naturally occurring atmospheric concentrations, plant leaves absorb significant quantities of ammonia. Porter et al. exposed air containing

^{15}N labeled NH_3 to corn seedlings in growth chambers. The soil-root system was isolated from the atmosphere by polyethylene bags which were tested and found to be impermeable to NH_3. At the conclusion of the testing period, the plants were analyzed and found to contain ^{15}N-enriched nitrogen compounds. They therefore deduced that direct foliar absorption was responsible for the presence of most of the ^{15}N found in the plant. They have indicated that simple isotopic exchange might account for a small part of the apparent [^{15}N] NH_3 uptake. They did not attempt to establish an uptake rate for NH_3 by these plants.

Hutchinson et al. (1972) based their estimates of the uptake rates of various plants on the difference in the mass flows of NH_3 and CO_2 out of the chamber before and after the plant was placed within the chamber. The soil was also isolated in these experiments. Measured absorption rates of NH_3 showed large diurnal fluctuations. Uptake rates at "night" were much lower than during light periods due to stomatal closure. Such rates for a given species showed little fluctuation even when nitrogen levels extant in the soils in which they grew were varied. Listed in Table XII are the NH_3 absorption rates for four crop species and for soybeans at three different nitrogen fertility levels.

Soil: The absorption of NH_3 by soils has received relatively little attention until recent years. Malo and Purvis (1964) investigated the seasonal variations in atmospheric NH_3 concentrations over New Jersey in relation to the rate of NH_3 absorption by six New Jersey soils. The atmospheric NH_3 content averaged 57 $\mu g/m^3$, considerably greater than the normal background concentration of about 4.2 $\mu g/m^3$. The excess atmospheric

Table XII. AMMONIA ABSORPTION RATES FOR FOUR CROP SPECIES AND FOR SOYBEAN AT THREE NITROGEN FERTILITY LEVELS

Species	Added soil nitrogen (mg)	Leaf area (cm^2)	NH_3 in chamber air ($\mu g/m^3$)	NH_3 uptake rate ($\mu g/m^2 \cdot hr$)
Soybean (Glycine max)	0	65	29	410.
Soybean (Glycine max)	5	80	24	420.
Soybean (Glycine max)	20	84	24	400.
Sunflower (Helianthus annuus)	5	96	31	490.
Corn (Zea mays)	5	58	24	560.
Cotton (Gossypium hirsutum)	5	55	44	350.

NH_3 in New Jersey is probably due to the combustion of coal, oil and gasoline. The rates of absorption by six soils under field conditions in New Brunswick are given in Table XIII, along with some soil characteristics.

The factors governing the amount of NH_3 absorbed by soils were investigated by Hanawalt (1969a,b). Hanawalt (1969a) tested the influence of several atmospheric factors on the sorption rate which included the length of exposure, the ambient NH_3 concentration, the ambient air temperature and the velocity of the air passing over the soil. The most important factor causing a change in sorption rates was the ambient NH_3 concentration. As the concentration increased from about 37 μg NH_3 - N/m^3 to about 67 μg NH_3 - N/m^3, the sorption rates

Table XIII. SOIL CHARACTER AND ABSORPTION RATES OF ATMOSPHERIC NH_3 UNDER FIELD CONDITIONS

Date and Soil	pH	Organic matter %	Clay %	C.E.C.** me/100g	NH_3 absorbed $g/m^2 \cdot day$
November 21, 1962					
1. Collington sandy loam	4.6	2.32	11.6	5.1	.008
2. Dutchess loam	5.4	7.12	26.3	12.7	.014
3. Lakewood sand	4.0	2.51	0.6	2.0	.006
February 18, 1963					
4. Matapeake silt loam	5.6	2.92	16.8	8.5	.026
5. Dutchess shale loam*	7.0	--	--	--	.009
6. Nixon loam*	5.7	--	--	--	.022

*Soils 5 and 6 both from cultivated fields

**Cation Exchange Capacity (C.E.C.) in milliequivalents per 100 grams

of the six soils tested were found to increase by about 40% to 75%. He also found increasing sorption rates to be correlated with increasing temperature, wind velocity or exposure time.

Hanawalt (1969b) evaluated the influence of several soil properties, such as organic matter, pH, cation exchange capacity, and texture and moisture on NH_3 sorption rates. The property found to most affect sorption rates was the soil moisture content, between which there was a positive correlation. Hanawalt concluded then that the rate with which NH_3 is absorbed by a soil is affected most "by those factors which affect

the rate of supply of ammonia to the soil surface," namely the atmospheric factors mentioned above, and "the fraction of the ammonia molecules which are actually captured," which is dependent upon the moisture content and air permeability of the soil.

Water Bodies: Because the absorption of atmospheric ammonia by lakes and streams can promote eutrophication in that water body, a great deal of concern has developed, especially in areas adjacent to large cattle feedlots and sewage treatment plants which both release great quantities of ammonia into the atmosphere. Hutchinson and Viets (1969) showed that the ammonia volatilized from cattle feedlots was absorbed by nearby water bodies. In their study, they calculated that Seeley Lake in northeastern Colorado, which is about 2 km from a 90,000 unit feedlot, absorbs enough NH_3 from the air over a one year period to elevate its nitrogen concentration by 0.6 mg/liter. An interesting result of their study was the discovery that although there was a tendency for the NH_3 content in precipitation to increase as the feedlots were approached, in no instance at any site, near or far from a feedlot, was the NH_3 content in precipitation very high. It appears that in all cases the amount of NH_3 removed from the atmosphere by precipitation was "insignificant compared to the amount absorbed directly from the air by aqueous surfaces in the vicinity of cattle feedlots" (see Table XIV).

In an attempt to quantify the removal of NH_3 released from a point source (such as from a plume produced by a sewage treatment plant) by an aqueous surface, Calder (1972) developed a simple mathematical model which takes into consideration the atmospheric transport and diffusion of the plume as well as a characterization of the removal process,

Table XIV. NH_3 - N ABSORBED BY SURFACE WATERS AND PRECIPITATION IN AREAS ADJACENT TO A CATTLE FEEDLOT

Site	Site description	NH_3 - N, $(kg/m^2) \times 10^4$		
		Absorption		Precipitation§
		Weekly*	Annual†	
1	No feedlots or irrigated fields within 3 km; no large feedlots or cities within 15 km	0.15	3.9	0.22
2	Only small (less than 200-unit) feedlots within 4 km, none closer than 0.8 km	.34	9.1	.29
3	About 0.2 km east of 800-unit feedlot and 0.6 km west northwest of another similar feedlot	.57	15	.32
4	On northeast shore of Clark Lake and 0.5 km southwest of 9,000-unit feedlot	.62	17	.29
5	On southeast shore of Seeley Lake and 2 km west northwest of 90,000-unit feedlot	1.3	34	.53
6	About 2 km east of 90,000-unit feedlot	1.3	34	.40
7	About 0.4 km west of 90,000-unit feedlot	2.8	73	.61

* Mean weekly absorption of ammonia-nitrogen by dilute acid traps during the period 27 July 1968 through 27 February 1969 (except sites 4 and 5, where measurement began 27 September 1968)

† Estimated annual absorption of NH_3 - N by water surfaces; calculated by dividing mean weekly rates by two and multiplying by 52 (weekly rates are divided by 2 because that is the ratio of NH_3 - N absorbed by dilute acid traps to lake water traps)

§ NH_3 - N in precipitation measured during the period 21 September through 21 November 1968. Total amount of p'pt. over this period was 2.2 cm at site 1 and between 3.0 and 3.6 cm at the other sites. Total quantity of NH_4^+ measured in the precipitation was extrapolated on an areal basis to give the measurements listed.

in this case the deposition velocity. The reader is referred to his article for the mathematical development of this model. Given the uncertainty in the value of the deposition velocity for NH_3 absorption by water, Calder concludes that absorption of NH_3 from an NH_3 cloud, passing over a water body some 30 km long at an average speed of 5 m/sec, could exceed 20 per cent.

Rainout and Washout: Ammonia, as previously mentioned, is extremely soluble in water. Once dissolved it ionizes to NH_4^+, the amount depending on the pH, as follows:

$$NH_3 \cdot H_2O \rightleftarrows NH_4^+ + OH^-$$

The rate constant equals 1.774×10^{-5} sec^{-1} (Robinson and Stokes, 1959). Normally the pH of cloud water ranges from 5 to 6. Under atmospheric conditions, assuming that an equilibrium solution is attained and CO_2 is present in normal concentrations, Junge (1963) has shown that approximately 87% of the NH_3 present in air at a concentration of 3 $\mu g/m^3$ could be absorbed in cloud droplets. Unfortunately, equilibrium is not usually, if ever, reached in cloud droplets.

Ammonia has been shown to be an important catalyst for the oxidation of SO_2 and NO_2 in solution (van den Heuval and Mason, 1963). Both Scott and Hobbs (1967) and Miller and de Pena (1972) have shown that as the partial pressure of NH_3 in the atmosphere increases, greater concentrations of SO_2 can be dissolved and oxidized in solution to form sulfate particles. The resulting aerosols, if evaporated, are composed largely of $(NH_4)_2SO_4$ particles with probably minor amounts of NH_4HSO_3, NH_4HSO_4 and $(NH_4)_2SO_3$ (Miller and de Pena, 1972). In the case where NH_3 is

co-absorbed with NO_2, the resulting particles would be composed primarily of NH_4NO_3.

It has been estimated (Robinson and Robbins, 1968) that almost 75% of atmospheric ammonia is removed from the atmosphere by conversion to NH_4^+ ions which condense in cloud droplets or particles and may evaporate to form aerosols. Georgii (1963) found that in a polluted air mass containing approximately 500 $\mu gSO_2/m^3$ and 10 $\mu gNH_3/m^3$, 98% of the ammonia is converted to $(NH_4)_2SO_4$ aerosols. McConnell (1973) has estimated that of a total NH_3 source strength of about 17.4×10^{10} kg NH_3 - N/yr, approximately 3×10^{10} kg of this ammonia is removed each year by rainout. He points out that this is a very conservative estimate and "may be low by as much as a factor of 3." Earlier, Robinson and Robbins estimated that 280×10^{10} kg NH_3 - N are removed each year by precipitation. On the whole, quantitative estimates are rather sparse and show a great discrepancy. To amend this, extensive measurements of the NH_4^+ content of rainwater must be made and analyzed.

Atmospheric Reactions Involving NH_3: Until just recently the reactions involved in the destruction of atmospheric ammonia were poorly defined. McConnell (1973) has suggested a number of reactions he believes to be significant in its destruction.

In the stratosphere the primary destructive reaction involves the photodissociation of NH_3 by sunlight with wavelengths greater than 2300 Å. The basic reaction is

$$NH_3 + h\nu \rightarrow NH_2 + H$$

The reaction rate is 1.3×10^{-4} sec^{-1}. The various excited NH_2 and NH states possible, together with their observed threshold wavelengths and their respective quantum yields are listed in McConnell's Table 1.

Great quantities of hydroxyl radicals are now believed to exist in the troposphere (Levy, 1971), the number density appearing to be on the order of about 10^{12} m^{-3} (McConnell et al., 1971). Reaction of NH_3 with these OH radicals in the troposphere and lower stratosphere is therefore possible, and, probably constitutes an important sink as well. The reaction is as follows:

$$NH_3 + OH \rightarrow NH_2 + H_2O$$

Stuhl (1973) records the rate as 1.5×10^{-19} m^3 sec^{-1} at room temperature. The magnitude of this rate constant is consistent with observations of Worley, Coltharp and Potter (1972) and Albers, Hoyermann, Wagner and Wolfrum (1969). McConnell points out that this same reaction can and probably does occur in the stratosphere, but it is not as effective there as photolysis. He further points out that although reactions of NH_3 with O, $O(^1D)$ and O_3 are possible, evidence suggests that such reactions would not play a significant role in the destruction of ammonia.

According to McConnell, "the most likely atmospheric products" of NH_3 destruction are N_2 and NO. In his paper he lists those reactions most likely to occur along with any information that might be available on their reaction rates. An anomaly exists here that cannot as yet be answered. As McConnell indicated, oxidation of NH_3 can be the source of a significant quantity of nitrogen oxides, especially NO (estimated at 7.04×10^{10} kg NO_x per year as N). But, he points out that the

magnitude of this NO source can be reduced due to a possible immediate reaction of NO with NH_2 producing N_2 and H_2O. This then would mean that oxidation of NH_3 could constitute a sink for NO. In effect then, oxidation of NH_3 can both produce and consume NO. The proportion of NO produced to that consumed by these reactions if they do occur is not as yet clear, but his contention is that the NO produced far outweighs that consumed.

Environmental Ammonia Cycle

Relatively little quantitative information is available on the strengths of both sources and sinks of ammonia. In fact, research into possible atmospheric oxidation reactions is so recent that any estimates made are subject to great uncertainty. Separate atmospheric ammonia cycles have never been constructed; its cycle is always considered together with that of nitrogen oxides. Because not very much is even known about the nitrogen oxides cycle, the uncertainty involved in the combined cycle must be very high.

To date the only nitrogen compound cycles devised are those of Robinson and Robbins (1968, 1970) and McConnell (1973) and a total geochemical nitrogen cycle of the present research. The first three cycles are compared in Table XV. The discrepancy among the three in source and sink estimates is immediately obvious. More research must be undertaken to provide us with a better understanding of the part ammonia plays in atmospheric chemistry and to quantify possible sources and sinks such as the oceans, lakes and vegetation.

Table XV. ATMOSPHERIC FLUXES INVOLVED IN VARIOUS AMMONIA CYCLES (in 10^{10} kg N/yr)

	Robinson & Robbins* (1968)	Robinson & Robbins (1970)	McConnell (1973)
I. Sources			
a. anthropogenic	---	.35	0.4
b. biological	670±	95.7	17
TOTAL	670	96.05	17.4
II. Sinks			
a. precipitation	280	18.6	3
b. dry deposition	70	4.9	7
c. oxidation to NO_x (troposphere)	N.E.	---	7
d. oxidation & photolysis to NO_x (stratosphere)	N.E.	---	0.04
e. gaseous deposition	90	74.9	---
TOTAL	440	98.4	17.04

N.E. = Mechanism recognized but no estimate made.

*NOTE: (see note in Table XI)

±Source strength here was adjusted by Robinson and Robbins to provide an additional amount of nitrogen needed to balance other portions of their nitrogen compound cycle.

GLOBAL NITROGEN CYCLE

The role which nitrogen compounds play in the chemistry of the atmosphere and earth is not well understood. A summary of what is known and has been suggested about the routes and rates of transport of these compounds is shown in Figure 4.

The diagram has been divided into certain spheres or reservoirs in which there exists an equilibrium concentration, or burden, of nitrogen. These burdens have recently been compiled and, in some cases, calculated by Wlotzka (1972). The only elaboration made upon his tabulations concerns the abundance of the nitrite and ammonium ion present in the ocean. Sverdrup, Johnson and Fleming (1942), as cited by Wlotzka, calculated the NO_3^- - N content of the ocean to be 5.7×10^5 Tg (5.7×10^{17} g). Emery, Orr and Rittenberg (1955)have estimated the total inorganic combined nitrogen content, that is, NO_3^-, NO_2^- and NH_4^+, to be 5.8×10^5 Tg. Therefore in this cycle the NO_2^- and NH_4^+ inventory of the hydrosphere has been set equal to 0.1×10^5 Tg. These burdens, shown encircled in their respective reservoirs in Figure 4, are given in units of Tg N (10^{12}g N).

There is so little quantitative data available concerning rates of transfer, or fluxes, of these compounds between reservoirs it is impossible to even attempt to balance this cycle. As a result the cycle suggests the possible routes of transfer and offers those fluxes which have been estimated. Fluxes are expressed in Tg N/yr (10^{12}g N/yr) and the direction of transport is indicated by arrows.

Details of the atmospheric portion of this cycle, with the exception of biological nitrogen fixation and denitrification as a source and sink of N_2 respectively, and the volcanic emanations of N_2, have been discussed

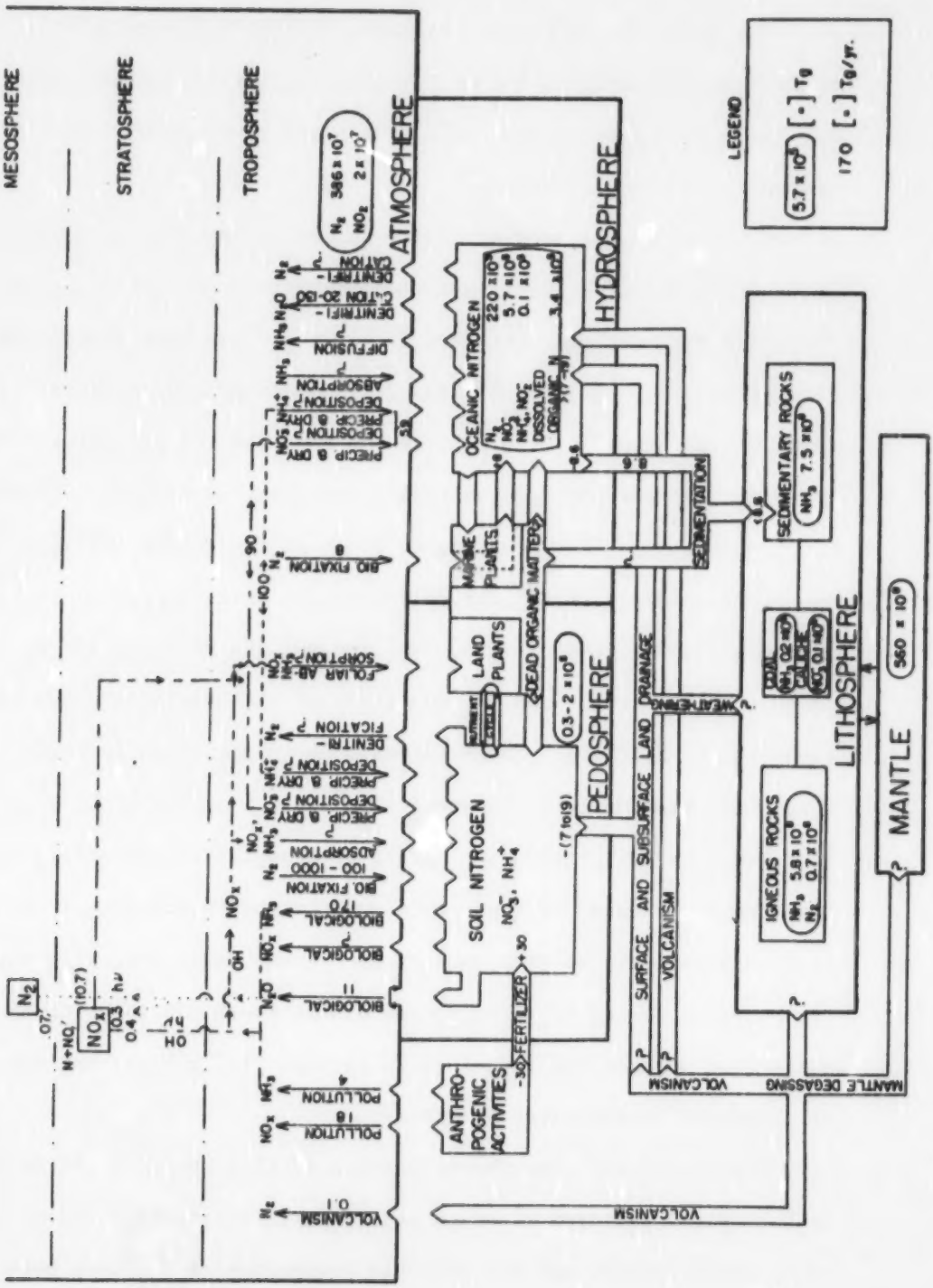

Figure 4. The Global Nitrogen Cycle.

in the previous sections concerning the sources and sinks of nitrogen oxides and ammonia. Nitrogen gas has been included in this cycle because the relationship between it and the other nitrogen compounds in the biosphere is so important in maintaining an equilibrium concentration of N_2 in the atmosphere.

The transport rates of the nitrogen oxides and ammonia in the atmospheric portion of the cycle, as well as the oxidation and photolysis scheme indicated are derived from McConnell (1973). Although he has estimated the total amount of NH_3 and NO_x removed by precipitation and dry deposition (100 and 90 Tg N/yr, respectively) on an annual basis, no differentiation was made between the amount removed over land and the amount removed over the ocean. Emery et al. (1955) estimated the contribution of NO_3^- and NH_4^+ to the sea by precipitation to total 59 Tg N/yr, and this is noted on the diagram.

In formulating a nitrogen budget of the ocean, Emery et al. (1955) also estimated that 8 Tg N/yr is added to the sea by biological nitrogen fixation, probably via some species of blue-green algae (Dugdale, 1972). An additional contribution to the total nitrogen reserves in the ocean is surface and subsurface land drainage. Emery has estimated that 19 Tg N/yr are added to the ocean by such land drainage while Wlotzka (1972) has calculated this contribution at 7 Tg N/yr.

The most widely recognized process which removes nitrogen from the ocean is sedimentation. The amount of nitrogen removed in this manner has been estimated to range from 5 Tg/yr (Wlotzka, 1972) to 8.6 Tg/yr (Emery et al , 1955). Other probable removal processes include denitrification, producing N_2 and N_2O, and diffusion of ammonia.

Liss and Slater (1974) calculated the flux of N_2O from the sea to the air at 38 Tg/yr (120 Tg N_2O/yr). Wlotzka estimated this flux to range between 20 and 130 Tg/yr. The amount of N_2 released from the ocean as a result of denitrification is unknown, as is the amount of NH_3 which escapes.

Nothing is known about the contributions of mantle degassing, volcanism, and weathering of the lithosphere to the total amount of nitrogen carried to the ocean by land drainage. It has been estimated though that about 0.1 Tg/yr is released to the atmosphere by volcanic activity.

A great deal of nitrogen containing fertilizers are applied each year to the soils across the world. Wlotzka recently estimated it to total 30 Tg/yr. Not only does this nitrogen play an important role in the nutrient cycle between soil and plants, but much of it is subject to leaching and would therefore contribute to the amount of nitrogen removed by surface and subsurface land drainage, ultimately to wind up in the sea.

As mentioned previously, the quantity of nitrogen present in the ocean is constant with time. Based on the nitrogen budget of sea water as formulated by Emery et al. (1955), Dugdale (1972) calculated the residence time of nitrogen in the ocean to be:

$$\tau = M/R = \frac{9.2 \times 10^5 \text{ Tg}}{86 \text{ Tg/yr}} \simeq 10^4 \text{ years}$$

or about 10,000 years which is an extremely short period of time on the geological time scale. For the sake of comparison, it was earlier calculated that the residence time of sulfate in the ocean is on the order of millions of years.

Figure 4 and the explanation above have attempted to show how very little is known about the global nitrogen cycle. Each question mark in the diagram needs to be replaced by a number representing an actual flux in the environment. Those fluxes that have been estimated need confirmation. Until all that is accomplished, any nitrogen cycle devised can only be, at best, conjectural.

OXIDANTS

OZONE

The problems involved when significant amounts of ozone are present in the atmosphere have come to light probably more as a result of the photochemical pollution problem in Los Angeles than from any other single factor. While background concentrations of ozone probably range from about 20-60 $\mu g/m^3$ (0.01-0.03 ppm), in urban centers like Los Angeles, it is not unusual to have O_3 present at levels greater than 500 $\mu g/m^3$ (.25 ppm). Ozone levels up to 400 $\mu g/m^3$ (0.2 ppm) usually will not cause any deleterious effects (Masters, 1971), but at concentrations of 600 $\mu g/m^3$ (0.3 ppm) ozone causes irritation of the mucous membranes in the nose and throat. At somewhat higher levels, it can cause coughing, choking and severe fatigue. When present at relatively high levels, such as those that occur in severe photochemical smogs, ozone causes bronchial irritation and interferes with normal lung functioning, causing breathing difficulty and chest pains. The highest ozone concentration detected in the Los Angeles atmosphere was 2,000 $\mu g/m^3$ (0.99 ppm) in 1956 (Chambers, as cited in Tebbens, 1968).

Another serious problem related to the occurrence of atmospheric ozone is its toxic effect on vegetation, especially field and forage crops (such as tobacco), leafy vegetables, shrubs, fruit and forest trees (particularly conifers).

Sources

The maximum ozone density occurs at an altitude of 25(±5) km, in the mid-stratosphere. This ozone though is not formed there but between 30 and 60 km where the following reaction proceeds:

$$O_2 + O + M \rightarrow O_3 + M$$

In this altitude range though ozone is relatively unstable. It may be destroyed either by collision with atomic oxygen to form molecular oxygen or by photolysis. The cycle is continuous; formation, destruction, formation. . . As a result an approximate state of equilibrium exists above about 40 km. The accumulation of ozone at 25 km is a result of its downward transport to a location where its destruction is less likely (Barry and Chorley, 1970).

Because the wavelengths of ultraviolet radiation that penetrates the troposphere are too long to cause photodissociation of oxygen, it has long been accepted that the presence of ozone in the troposphere is due primarily to the transport of ozone down from the stratosphere. The amount present in the troposphere would then be related to the injection rate through the tropopause, estimated as ranging between 1.9 and 7.5 x 10^3 kg/yr (Junge, 1962).

Recently, Chameides and Walker (1973) proposed a model wherein both seasonal and diurnal variations in the tropospheric ozone density are assumed to be caused by photochemical changes rather than a change in the flux of stratospheric ozone-rich air into the troposphere.

Their model calls for the production of O_3 by the methane oxidation scheme suggested by Crutzen (1973). The oxidation of methane produces hydroperoxyl radicals which then react with nitric oxide:

$$HO_2 + NO \rightarrow OH + NO_2 \text{ followed by} \qquad (1)$$

$$NO_2 + h\nu \rightarrow NO + O \text{ and} \qquad (2)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (3)$$

At 27°C, k_2 is about 5 x 10^{-19} m^3 sec^{-1} (Levy, 1973a). Based on calculated atmospheric densities of HO_2 and NO_2, Chameides and Walker calculated an ozone production rate of approximately 5 x 10^{12} m^{-3} sec^{-1}, and photochemical lifetimes of a few tenths of a day near the ground, of one day at 5 km, and 10 days at 10 km. They concluded that ozone is in a state of photochemical equilibrium in the troposphere.

Upon developing a photochemical model of reactions affecting the density of tropospheric ozone, they found they could satisfactorily reproduce the seasonal variations found in ambient ozone densities (see Figure 5) by applying their model to temperature and relative humidity conditions typical of winter and summer. By analyzing the specific effects that lowering the temperature, humidity and photodissociation rates each make in altering the summer profile to one characteristic of the winter, they conclude that decreasing the photodissociation rates alone causes a realistic alteration of the summer profile to that of winter (Figure 6). This model shows that photochemical processes rather than the vertical transport of O_3-rich air can be responsible for the presence of ozone in the troposphere. It also presents a challenge for other researchers to prove whether or not most tropospheric ozone originates in the stratosphere as commonly believed or in the troposphere by the reactions these authors propose.

Removal Mechanisms

Ozone is relatively insoluble in water; at 20°C and 1 atm its solubility is 0.052 g/100g H_2O. Therefore, removal of ozone from the atmosphere

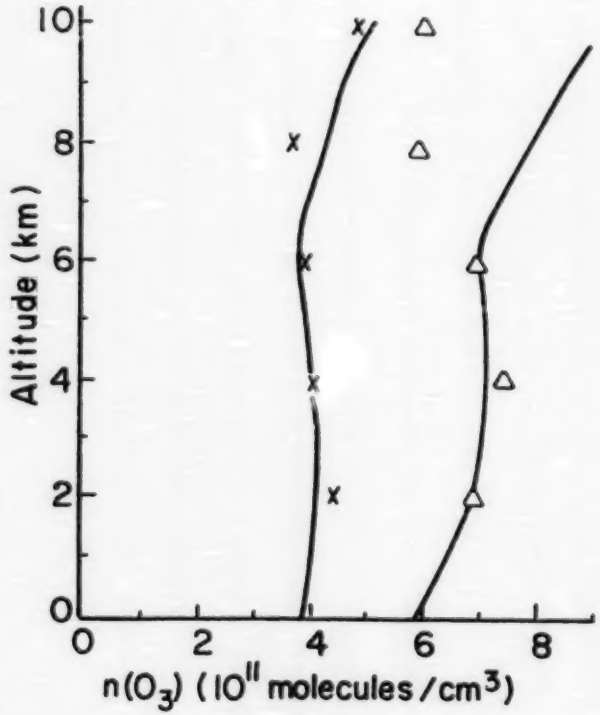

Figure 5. Summer and winter ozone profiles at 30°N.

(legend) —— calculated*
Δ summer } measured†
x winter }

*densities calculated by Chameides & Walker (1973)

†densities measured by Hering & Borden (1964)

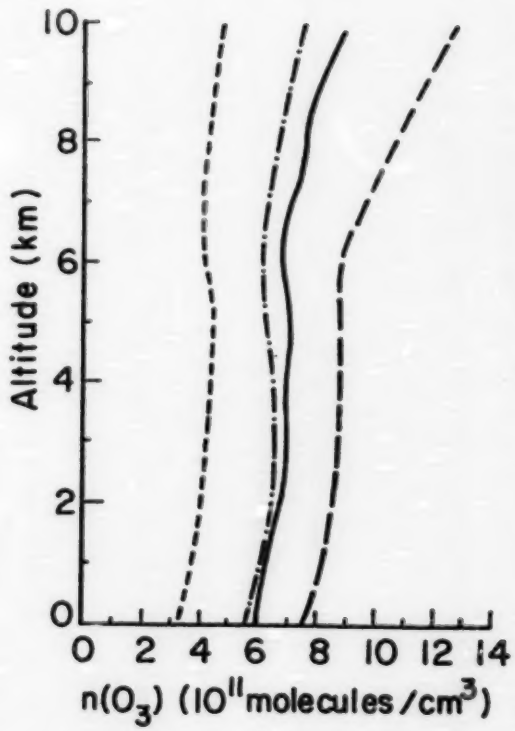

Figure 6. The effects of some meteorological parameters on the ozone profile.

(legend) —— calculated, summer, 30°N
– – temperature decreased by 5%
-·- H_2O vapor density decreased by 5%
--- photodissociation rates decreased to their winter values

by washout and rainout can be disregarded. There is evidence though that ozone is removed by the oceans. Ozone is also absorbed by vegetation and soil and these appear to represent major sinks, for O_3. Due to its nature as a strong oxidizing agent, ozone participates in a number of atmospheric reactions, especially in polluted atmospheres. Junge (1962) has estimated the tropospheric residence time of ozone to range between 3 and 4 months.

Vegetation: Ozone has caused a great deal of damage to vegetation in the United States and its effects on both plants and the economy have been well documented (Rich, 1964 and Millecan, 1971). When ozone is present in the atmosphere at low concentrations, vegetation is capable of absorbing some without inflicting damage upon itself. Hill (1971) showed that an alfalfa canopy removed ozone from his experimental chamber at a rate of 1.7 cm/sec. In this study the threshold level above which the plants sustained injury was 4.16×10^{-4} mol/m^3 (200 µg/m^3 or 0.1 ppm). Previously, Hill and Littlefield (1969) had shown that high concentrations of ozone can cause stomatal closure in the leaf thereby reducing the uptake of ozone. Unfortunately in Hill's study the injury threshold limit of alfalfa was 4.16×10^{-4} mol/m^3 which was also the level above which the stomates began to close. As a result, the effect of stomatal closure on ozone uptake rates could not be adequately evaluated.

The hypothesis that the uptake of O_3 is dependent on the degree of stomatal opening received additional support by Rich, Waggoner and Tomlinson (1970) as a result of their experiments on bean plants. They concluded that ozone follows the same but reverse path as that of water vapor which is transpired by the leaf. The water vapor originates from

saturated cells directly beneath the stomata and is released when the stomata are open. Conversely, the ozone travels through the open stomata onto the surface of the substomatal cells where it is reduced to very low concentrations. Hill points out that although ozone's solubility in water is not very high, it breaks down relatively rapidly and therefore a fairly high uptake rate is to be expected.

Soil and Water Bodies: The ground has long been recognized as a sink for ozone. Over the last two decades several estimates of the vertical flux of O_3 into the ground have been made. Junge (1962) tabulated the estimates made through 1962 [see his Table I]. For the most part, the estimates range from about 3 to 200 x 10^{-12} kg $O_3/m^2 \cdot sec$. Junge calculated the flux density to be 60 x 10^{-12} $kg/m^2 \cdot sec$ which is in good agreement with the estimate of 48 x 10^{-12} $kg/m^2 \cdot sec$ made by Kroening and Ney (1962). These measurements of O_3 into the ground include destruction by both soil and vegetation. No attempts were made to differentiate the ozone destroyed by each, and no suggestions were offered as to what the exact reason for the destruction at these surfaces were.

Aldaz (1969) was the first to offer data on the ozone flux into various surfaces: soil, vegetation, snow and water (Figure 7). These fluxes were determined assuming a partial ozone density of 40 $\mu g/m^3$ (0.02 ppm, or natural background concentration levels). Using an equation analogous to that used by Liss and Slater (1974) to estimate the flux of a gas across the air-sea interface, Aldaz calculated the flux of O_3 into both the terrestrial and marine portions of the northern and southern hemispheres. The equation used to determine the ozone flux is

$$F = 1.25 \times 10^{10} \, kq \quad ,$$

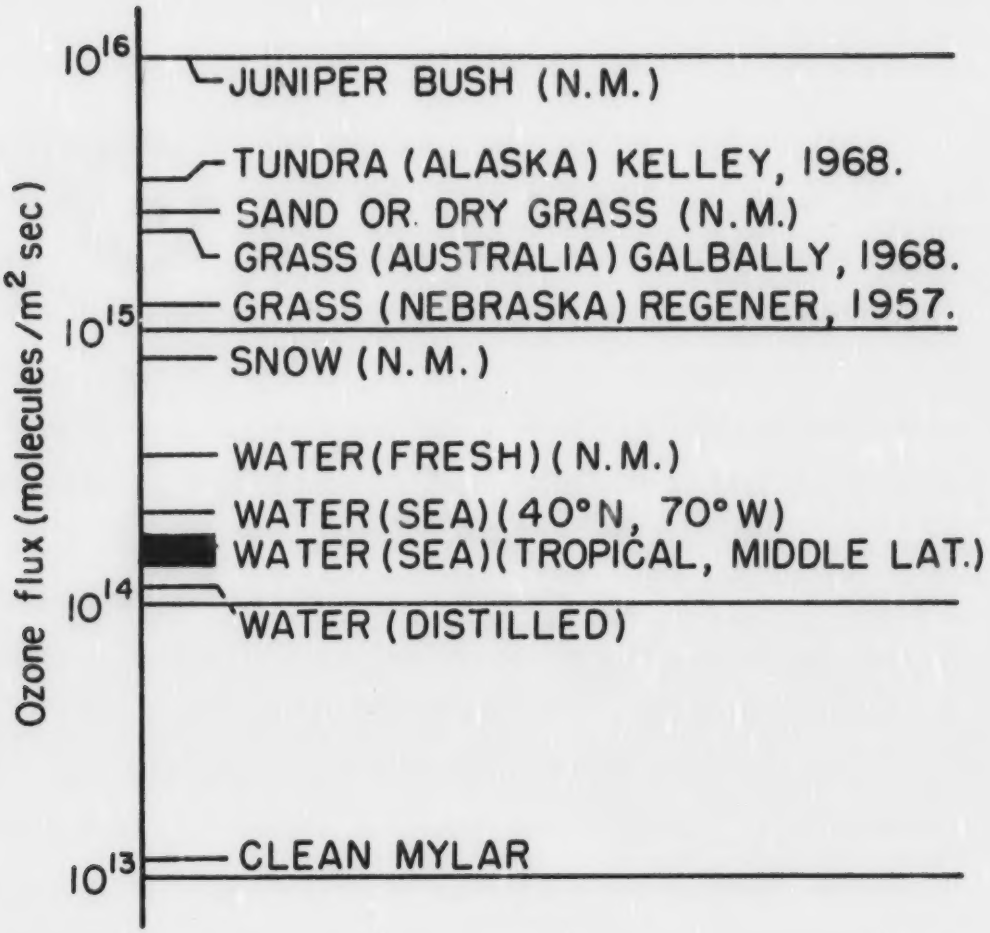

Figure 7. Ozone fluxes into different surfaces assuming a partial ozone density of 40 $\mu g/m^3$.

where q is the partial density of O_3 in $\mu g/m^3$, and k, the reaction constant, is a measure of the chemical reactivity of the surface to ozone. In essence then, k is actually a deposition velocity term. The reaction constants used were 0.60 cm/sec over land, 0.04 cm/sec over water and 0.0? cm/sec over snow. Data Aldaz used to compute the global ozone sink is given in Table XVI. Because there are no measurements of ozone uptake by tropical vegetation, Aldaz assumes in estimate (A) that the rate of destruction in the tropics is equal to that in other land regions, and in (B) he assumes a destruction rate 5 times greater in the tropics than in other land regions. In conclusion, he found the sink strength of the earth's surface to lie between 1.3 and 2.1 x 10^{12} kg/yr. He also showed that destruction of ozone by New Mexican soils is about 15 times faster than over the Atlantic Ocean (Figure 7), and that bare, dry soil destroyed approximately 75% more O_3 than when moist. It must be pointed out that the means by which the soil destroys ozone was not identified.

Turner, Rich and Waggoner (1973) recently found that a bare, freshly cultivated, fine sand loam removed ozone at a rate varying from .5 - 2 x 10^{-8} $mol/m^2 \cdot sec$ when present in the atmosphere at concentrations ranging from 64-208 $\mu g/m^3$. They also found that as the soil moisture content was increased, the resistance of the soil to O_3 removal also increased. As mentioned above, Aldaz found a similar situation to exist in the sand loam soil he tested in New Mexico; i.e., as the soil moisture increases, ozone destruction by the soil decreases.

Atmospheric Reactions Involving O_3: Although reactions of ozone with natural contaminants such as terpene do occur (Rasmussen and Went, 1965; and Ripperton et al., 1967), its importance arises from the

Table XVI. ESTIMATE OF THE EARTH'S SINK STRENGTH FOR ATMOSPHERIC OZONE WITH RELATED DATA

LATITUDE	SOUTH				NORTH			
	90° - 60°	60° - 30°	30° - 15°	15° - 0°	0° - 15°	15° - 30°	30° - 60°	60° - 90°
Water[a]	4	17	9	10	10	8	9	3
Land[a]	3	1	3	3	3	4	9	4
Ozone density[b]	45	50	35	35	35	45	55	40
Flux over water[c]	3.8	4.15	3.0	3.0	3.0	3.8	4.65	3.3
Flux over land[c]	1.8[f]	62.3	43.5	43.5	43.5	56.15	68.4	5.0
Water sink[d]	.83	3.65	1.32	1.49	1.49	1.49	2.16	.5
Land sink[e] (A)	.33[f]	3.16	6.64	6.64	6.64	11.46	31.4	10.13
Land sink[e] (B)	.33[f]	3.16	6.64	33.2	33.2	11.46	31.4	10.13

Total hemispheric values (in units of 10^5 mol/sec):

Southern hemisphere (A), 24.9 Northern hemisphere (A), 64.8
Southern hemisphere (B), 51.5 Northern hemisphere (B), 91.4

Global (A), 89.7×10^5 mol/sec = 1.3×10^{12} kg/yr
Global (B), 142.9×10^5 mol/sec = 2.1×10^{12} kg/yr

[a] Water and land in percent of earth's surface (5.1×10^{18} cm^2)

[b] Surface ozone density in $\mu g/m^3$

[c] Flux of ozone in units of 10^{-10} $mol/m^2 \cdot sec$

[d] Sink strength of water surfaces in units of 10^5 mol/sec

[e] Sink strength of land surfaces in 10^5 mol/sec, under assumptions (A) and (B) as explained in text

[f] Complete snow cover assumed for Antarctica

photochemical reactions in which it participates in polluted atmospheres; namely the photo-oxidation of hydrocarbons in the presence of nitrogen dioxide. The initial oxidation of olefins by ozone for instance can lead to a long series of reactions which produce ketones, aldehydes, organic acids and nitrogen-containing compounds such as peroxyacetylnitrate (PAN). The presence of these compounds in the atmosphere has been shown to be the cause of considerable eye irritation (Schuck and Doyle, 1959). Rate constants for the reaction of ozone with numerous hydrocarbons have been summarized by Altshuller and Bufalini (1971) and Bufalini and Altshuller (1965). Because the reactions of ozone in polluted atmospheres are so numerous and have been the subject of extensive investigation and review, it would not serve the best interest of this paper to review these reactions here. For additional information the reader is referred to Hecht and Seinfeld (1973), Dütsch (1971), Ripperton and Vukovich (1971), Stephens (1969), Altshuller and Bufalini (1965), and Leighton (1961).

ORGANIC GASES

Organic gases constitute the second major group of air contaminants. This group includes all classes of hydrocarbons and those formed when some of the hydrogen of the original compound is replaced by other substituent groups containing nitrogen, sulfur, or oxygen. Organic gases are further subdivided into reactive and non-reactive classes. Among these classes only hydrocarbons are considered here. The more important reactive hydrocarbons include the olefins and aromatics. Paraffinic hydrocarbons are classified as non-reactive.

REACTIVE HYDROCARBONS

Because of their role in photochemical reactions in polluted atmospheres, reactive hydrocarbons have been the subject of great interest. These photochemical reactions produce smog which is associated with eye and respiratory tract irritation, reduced atmospheric visibility, and plant damage.

Limited ambient data from Point Barrow, Alaska (Robinson and Robbins, 1968) indicate that ethylene, the most abundant hydrocarbon of this group, is present at a concentration of less than 1 $\mu g/m^3$ (less than 1 ppb). In the absence of other ambient measurements one might consider the concentration of ethylene measured at the above location to represent the upper limit of the background concentration for components in this group.

Sources

A variety of hydrocarbons are released to the atmosphere as a result of both anthropogenic activity and natural processes. The most important

anthropogenic source of hydrocarbons is motor vehicle exhaust from the incomplete combustion of fuel. Robinson and Robbins (1968) estimate that the total annual emission of olefins and aromatics from the combustion of various fuels is 27×10^9 kilograms. A bibliography of various emission sources has been compiled by the U.S. Department of Health, Education and Welfare (1970).

Plant species also release appreciable quantities of volatile organic substances to the surrounding air. The major reactive hydrocarbons emitted by trees are ethylene, monoterpene (C_{10}), and isoprene (C_5). In a recent study, Rasmussen (1972) concluded that the forests represent a global natural source of 175×10^9 kg of reactive hydrocarbons each year. This emission rate is 6 times greater than that estimated for reactive hydrocarbons of anthropogenic origin.

Removal Mechanisms

Hydrocarbons in general are not water soluble, and therefore, they cannot be directly removed from the atmosphere by wet processes such as washout and absorption by surface waters. Various studies have shown that photochemical reactions are important in removing reactive hydrocarbons, although the products formed may cause detrimental side effects such as eye and throat irritation. This class of hydrocarbons, upon their emission into the atmosphere undergo rapid chemical transitions in the presence of: atomic oxygen and ozone (Bufalini and Altshuller, 1965); oxides of nitrogen (Schuck, 1961; Alley, Martin and Ponder, 1965); ozone and sulfur dioxide (Cox and Penkett, 1971b) and; nitrogen dioxide and sulfur dioxide (Schuck and Doyle, 1959).

The basic kinetic mechanisms of hydrocarbon reactions in the atmosphere are given by Hecht and Seinfeld (1972). These authors present a 15-step mechanism for photochemical smog formation, with rate constants and stoichiometric coefficients chosen according to the particular hydrocarbons involved in the reactions and the initial reactant ratios. The state of the art of photochemical reactions is analyzed by Dodge (1973) and Seinfeld, Hecht and Roth (1973). The reader is referred to these publications for an up-to-date view.

Quantitative data on the rates of these atmospheric reactions are rare. The limited data available as reported by Hidy (1973) suggests that 1-10% by weight of the reactive hydrocarbons emitted into the atmosphere are converted to aerosols and eventually removed by scavenging or deposition. The remaining hydrocarbons are eventually oxidized to carbon dioxide and water vapor.

Smith et al. (1973) investigated the capacity of soils to absorb ethylene and acetylene. Sterilized and air-dried unsterilized soils removed neither of these hydrocarbons from the test chamber. Moist unsterilized soils (50% saturated) did reduce the ambient concentrations of these gases although the uptake rate was relatively slow compared to the other gases they studied (SO_2 and CO). They concluded, as did Abeles et al. (1971) in an experiment on ethylene uptake by soil, that the sorption of both ethylene and acetylene is due to microbial activity in the soil. Smith et al. found that the soils they tested removed ethylene at average rates ranging from $.14-.97 \times 10^{-9}$ mol per gram of soil per day (mol/g•d) and acetylene from $.24-3.12 \times 10^{-9}$ mol/g•d.

NON-REACTIVE HYDROCARBONS

This group, which consists of methane and the higher saturated hydrocarbons, has been found to be much less involved in photochemical reactions and smog formation than reactive hydrocarbons. By far the most abundant paraffinic hydrocarbon in the atmosphere is methane. Methane's background concentration is about 1000 $\mu g/m^3$ (1.5 ppm), while the background concentration for heavier gases in this class is less than 1 $\mu g/m^3$ (less than 1 ppb) (Robinson and Robbins, 1968).

Sources

The anthropogenic source of paraffinic hydrocarbons is the incomplete combustion of fuel in motor vehicles. The annual emission of paraffinic hydrocarbons is estimated to be 60×10^9 kg (Robinson and Robbins, 1968).

Among natural sources approximately 310×10^9 kg of methane is produced annually in swamps and various water bodies as a result of bacterial decomposition. The relatively high concentration of methane in the atmosphere compared to other organic gases is related to this natural process.

Removal Mechanisms

Because they are so insoluble in water, paraffinic hydrocarbons can not be removed from the atmosphere by wet processes. The primary sink for methane in the troposphere is its oxidation by hydroxyl radicals to form carbon monoxide. The initial reaction is as follows:

$$CH_4 + OH \rightarrow CH_3 + H_2O$$

The rate coefficient for this equation equals 5.5×10^{-12} exp (-1900/T) (Greiner, 1970). For a complete development of this oxidation scheme the reader is referred to Levy (1971), McConnell et al. (1971) and Levy (1972, 1973a). Based upon density profiles of CH_4 and hydroxyl radicals in the troposphere, and the rate equation given above, Levy (1973b) calculated the average daily loss of methane at a particular altitude. The total column loss rate for methane was found to be 7.48×10^{-8} $mol/m^2 \cdot sec$. This results in a tropospheric residence time for methane of 2 years.

Rasmussen, Hutton and Garner (1968) and Robinson and Robbins (1968) have also suggested that the volatile organic components of the atmosphere are removed by bacteriological processes and vegetation. However, quantitative data and rate equations for these removal mechanisms are nonexistant at present.

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